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(54) **MULTIBLOCK COPOLYMER, RUBBER COMPOSITION, AND TIRE**

(57) A multiblock copolymer, obtainable by copolymerization of a conjugated diene compound and a non-conjugated olefin, is characterized in that: a structure of the multiblock copolymer includes A-(B-A)_x and/or B-(A-B)_x, wherein "A" represents a block portion constituted of monomer units of a non-conjugated olefin, "B" represents a block portion constituted of monomer units of a conjugated diene compound, and "x" represents an integer ≥ 1 ; content of the non-conjugated olefin portion

is ≤ 50 mol %; 0 mol % < crystal content of the non-conjugated olefin portion ≤ 20 mol %; and 0 % < degree of crystallinity of the non-conjugated olefin portion ≤ 40 %. Vulcanized rubber having high fracture resistance and high crack resistance (thus a rubber composition and a tire each using the vulcanized rubber and having such excellent physical properties) can be manufactured from the multiblock polymer.

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Description

TECHNICAL FIELD

5 **[0001]** The present invention relates to a multiblock copolymer, a rubber composition, and a tire.

BACKGROUND ART

10 **[0002]** Tires having high durability have been increasingly requested in recent years, responding to social demand for saving energy and resources. In view of these requests, there has been an increasing preference for a rubber material excellent in fracture resistance and weather resistance. In general, diene-based rubber such as butadiene rubber (BR), styrene-butadiene rubber (SBR), and the like are excellent in fracture resistance but do not have satisfactory weather resistance (examples of weather resistance include crack resistance, i.e. resistance to crack generation due to aging caused by ozone, deterioration over time, or the like). Non diene-based rubber such as ethylene-propylene rubber (EPM),
15 ethylene-propylene-diene rubber (EPDM), butyl rubber (IIR), and the like on the other hand are excellent in weather resistance but do not have satisfactory fracture resistance equivalent to diene-based polymer, thereby narrowing a range of applications thereof. Mixing diene-based rubber and non diene-based rubber in use has been attempted to achieve high fracture resistance and high weather resistance in a compatible manner (PTL 1) but fracture resistance does not satisfactorily improve in this case.

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CITATION LIST

Patent Literature

25 **[0003]** PTL 1: USP 4,645,793

SUMMARY

30 **[0004]** In view of this, an object of the present disclosure is to provide: a multiblock copolymer and a rubber composition from which vulcanized rubber having high fracture resistance and high crack resistance can be obtained; and a tire having high fracture resistance and high crack resistance.

[0005] A multiblock copolymer of the present disclosure is a multiblock copolymer obtainable by copolymerization of a conjugated diene compound and a non-conjugated olefin, wherein:

35 a structure of the multiblock copolymer includes $A-(B-A)_x$ and/or $B-(A-B)_x$, wherein "A" represents a block portion constituted of monomer units of a non-conjugated olefin, "B" represents a block portion constituted of monomer units of a conjugated diene compound, and "x" represents an integer ≥ 1 ;
content of the non-conjugated olefin portion is ≤ 50 mol %;
0 mol % < crystal content of the non-conjugated olefin portion ≤ 20 mol %; and
40 0 % < degree of crystallinity of the non-conjugated olefin portion ≤ 40 %. According to the multiblock copolymer of the present disclosure, it is possible to obtain vulcanized rubber having high fracture resistance and high crack resistance.

45 **[0006]** In the multiblock copolymer of the present disclosure, the content of the non-conjugated olefin portion is preferably in the range of 10 mol % to 40 mol %. Fracture resistance and crack resistance of resulting vulcanized rubber can be further enhanced by this structure.

[0007] In the multiblock copolymer of the present disclosure, the crystal content of the non-conjugated olefin portion is preferably in the range of 5 mol % to 15 mol %. Fracture resistance and crack resistance of resulting vulcanized rubber can be further enhanced by this structure.

50 **[0008]** In the multiblock copolymer of the present disclosure, the degree of crystallinity of the non-conjugated olefin portion is preferably in the range of 15 % to 40 %. Fracture resistance and crack resistance of resulting vulcanized rubber can be further enhanced by this structure.

[0009] A rubber composition of the present disclosure characteristically uses the aforementioned multiblock copolymer as a rubber component. According to the rubber composition of the present disclosure, it is possible to obtain vulcanized
55 rubber having high fracture resistance and high crack resistance.

[0010] A tire of the present disclosure characteristically uses the aforementioned rubber composition. As a result, the tire has high fracture resistance and high crack resistance.

[0011] According to the present disclosure, it is possible to provide: a multiblock copolymer and a rubber composition

from which vulcanized rubber having high fracture resistance and high crack resistance can be obtained; and a tire having high fracture resistance and high crack resistance.

DETAILED DESCRIPTION

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[0012] An embodiment of the present disclosure will be described hereinafter.

[Multiblock copolymer]

10 **[0013]** A multiblock copolymer of the present disclosure is a multiblock copolymer obtainable by copolymerization of a conjugated diene compound and a non-conjugated olefin, wherein: a structure of the multiblock copolymer includes A-(B-A)_x and/or B-(A-B)_x, wherein "A" represents a block portion constituted of monomer units of a non-conjugated olefin, "B" represents a block portion constituted of monomer units of a conjugated diene compound, and "x" represents an integer ≥ 1; content of the non-conjugated olefin portion is ≤ 50 mol %; 0 mol % < crystal content of the non-conjugated olefin portion ≤ 20 mol %; and 0 % < degree of crystallinity of the non-conjugated olefin portion ≤ 40 %. Hereinafter, a "block portion A" constituted of monomer units of a non-conjugated olefin and a "block portion B" constituted of monomer units of a conjugated diene compound will occasionally be referred to as a "non-conjugated olefin block portion" and a "conjugated diene compound block portion", respectively.

20 **[0014]** Whether or not the copolymer is a multiblock copolymer having the A-(B-A)_x structure and/or the B-(A-B)_x structure, i.e. whether or not the copolymer has a block portion A constituted of monomer units of a non-conjugated olefin and a block portion B constituted of monomer units of a conjugated diene compound, can be confirmed by, for example, proving that the multiblock copolymer includes a non-conjugated olefin portion therein and that there exist crystals of a non-conjugated olefin block in the non-conjugated olefin portion by NMR. Specifically, it is possible to confirm that the multiblock copolymer includes a non-conjugated olefin portion therein by detecting a peak derived from a non-conjugated olefin block through measurement of ¹³C-NMR spectra. Further, it is possible to confirm that there exist crystals of a non-conjugated olefin in the non-conjugated olefin portion by: measuring a FID (free induction decay) signal by using a time-domain NMR (TD-NMR) analyzer according to the MSE (magic sandwich echo) method; determining crystal content of the non-conjugated olefin portion in the non-conjugated olefin portion; and checking whether the crystal content exceeds zero or not. In a case where a copolymer includes a non-conjugated olefin portion therein but existence of crystals of a non-conjugated olefin block cannot be detected, it is judged that the copolymer is not a multiblock copolymer but a random copolymer.

25 **[0015]** In the present disclosure, "content of a non-conjugated olefin portion" represents mole percent (mol %) of a block portion constituted of monomer units of a non-conjugated olefin in a multiblock copolymer. The multiblock copolymer can exhibit high weather resistance when it has a block portion constituted of monomer units of a non-conjugated olefin at mole percent in the range of > 0 mol % and ≤ 50 mol %. Further, since the multiblock copolymer also has a block portion constituted of monomer units of a conjugated diene compound, the multiblock copolymer can function as elastomer and be subjected to cross-linking by sulfur, so that it successfully exhibits a high elongation at fracture and thus high fracture resistance.

30 **[0016]** Content of the non-conjugated olefin portion can be determined by, for example: measuring ¹³C-NMR spectra of the multiblock copolymer; and obtaining an integration ratio of a peak derived from a non-conjugated olefin block and a peak derived from a conjugated diene compound block, to calculate content of the non-conjugated olefin portion based on the integration ratio. The content of the non-conjugated olefin portion can be controlled by, for example, controlling charging amounts of non-conjugated olefin monomers and/or conjugated diene compound monomers in a method for manufacturing a multiblock copolymer described below.

35 **[0017]** In the present disclosure, "crystal content of a non-conjugated olefin portion" represents mole percent (mol %) of crystals of a block portion constituted of monomer units of a non-conjugated olefin in a multiblock copolymer. The multiblock copolymer can avoid crack generation due to orientation of non-conjugated olefin crystals therein when crystal content of the non-conjugated olefin portion in the multiblock copolymer is in the range of > 0 mol % and ≤ 20 mol %.

40 **[0018]** The crystal content of a non-conjugated olefin portion can be determined by, for example: measuring a FID (free induction decay) signal by using a time-domain NMR (TD-NMR) analyzer according to the MSE (magic sandwich echo) method; and subjecting the FID signal to fitting by the analytical equation shown below.

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$$G(t) = f_c \cdot \exp\{-0.5(at)^2\} \cdot \sin(bt)/bt + f_i \cdot e^{(t/T_{2i})^{1/v_a}} + f_m \cdot e^{(t/T_{2m})^{1/v_i}}$$

55 wherein $f_c + f_i + f_m = 1$, f_c : proportion of crystals of a non-conjugated olefin portion (1 H%), f_i : proportion of intermediate phase (1 H%), f_m : proportion of soft phase (1 H%)

[0019] Setting of a pulse program and an analytical method associated therewith may follow the teachings described in the following reference: Kerstin Schaefer, *Macromolecules* 2013, 46, pp. 7818-7825; and Henriette W. Meyer, *Polymer Journal* (2012) 44, pp. 748-756. Crystal content of a non-conjugated olefin portion can be controlled by, for example, controlling or changing conditions such as charging amounts of non-conjugated olefin monomers and/or conjugated diene compound monomers, the order of charging the respective monomers, the number of charging the respective monomers, type of a polymerization catalyst, and the like in a method for manufacturing a multiblock copolymer described below.

[0020] In the present disclosure, "degree of crystallinity of a non-conjugated olefin portion" represents a proportion (%) taken up by crystals of a block portion constituted of monomer units of a non-conjugated olefin in a multiblock copolymer. The multiblock copolymer can avoid concentration of stress on a hard olefin portion, while improving strength by exhibiting static crystallinity to some extent, when degree of crystallinity of the non-conjugated olefin portion in the multiblock copolymer is in the range of $> 0\%$ and $\leq 40\%$.

[0021] Accordingly, content of a non-conjugated olefin portion is $\leq 50\text{ mol } \%$; $0\text{ mol } \% <$ crystal content of the non-conjugated olefin portion $\leq 20\text{ mol } \%$; and $0\% <$ degree of crystallinity of the non-conjugated olefin portion is $\leq 40\%$ in our multiblock copolymer, whereby it is possible, when vulcanized rubber is to be manufactured by using the multiblock copolymer, to provide a rubber composition from which vulcanized rubber having high fracture resistance and high crack resistance can be obtained.

[0022] Content of a non-conjugated olefin portion in the multiblock copolymer is preferably in the range of $10\text{ mol } \%$ to $40\text{ mol } \%$. The content of a non-conjugated olefin portion $\geq 10\text{ mol } \%$ ensures satisfactory fracture resistance and crack resistance of the multiblock copolymer. The content of a non-conjugated olefin portion $\leq 40\text{ mol } \%$ ensures that a conjugated diene compound block portion, which contributes to improvement of elongation at fracture, can exist in a satisfactory content in the multiblock copolymer.

[0023] Crystal content of a non-conjugated olefin portion in the multiblock copolymer is preferably in the range of $5\text{ mol } \%$ to $15\text{ mol } \%$. The crystal content of a non-conjugated olefin portion $\geq 5\text{ mol } \%$ ensures satisfactory presence of static crystallinity, which contributes to improvement in strength, in the multiblock copolymer. The crystal content of a non-conjugated olefin portions $\leq 15\text{ mol } \%$ can prevent concentration of stress on a hard olefin portion from occurring.

[0024] Degree of crystallinity of a non-conjugated olefin portion in the multiblock copolymer is preferably in the range of 15% to 40% . The degree of crystallinity of a non-conjugated olefin portion $\geq 15\%$ ensures satisfactory presence of static crystallinity, which contributes to improvement in strength, in the multiblock copolymer. The degree of crystallinity of a non-conjugated olefin portion $\leq 40\%$ can reliably prevent concentration of stress on a hard olefin portion from occurring. The degree of crystallinity of a non-conjugated olefin portion can be controlled by, for example, controlling or changing conditions such as charging amounts of non-conjugated olefin monomers and/or conjugated diene compound monomers, the order of charging the respective monomers, the number of charging the respective monomers, type of a polymerization catalyst, and the like in a method for manufacturing a multiblock copolymer described below.

[0025] Our multiblock copolymer preferably has weight average molecular weight (Mw) in terms of polystyrene in the range of 50,000 to 600,000, although the Mw is not particularly limited thereto. The weight average molecular weight in terms of polystyrene $\geq 50,000$ ensures high fracture resistance and high weather resistance of the multiblock copolymer. The weight average molecular weight in terms of polystyrene $\leq 600,000$ ensures good workability, as well as high fracture resistance and high weather resistance, of the multiblock copolymer. Weight average molecular weight in terms of polystyrene can be determined by gel permeation chromatography (GPC) by using polystyrene as the standard substance. Weight average molecular weight in terms of polystyrene, of the multiblock copolymer, can be controlled by, for example, controlling conditions such as reaction time for copolymerization, type of a promoter, and the like in a method for manufacturing a multiblock copolymer described below.

[0026] Boundaries between respective block portions (A-B), (B-A) need not be clearly distinguished in the multiblock copolymer. Accordingly, for example, a portion constituted of a mixture of a conjugated diene compound and a non-conjugated olefin, e.g. a random structure and/or a taper structure, may be formed between a block portion A and a block portion B. Further, type, composition and the like of monomers constituting one block portion may be different from those constituting another block portion among block portions belonging to the same category (A or B).

[0027] Examples of a conjugated diene compound include 1,3-butadiene, isoprene, 1,3-pentadiene, 2,3-dimethylbutadiene, and the like, without being particularly limited thereto. 1,3-butadiene and isoprene are preferable among these examples. These examples of the conjugated diene compounds may be used either solely or in combination of two or more types.

[0028] Examples of a non-conjugated olefin include α -olefins such as ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, and 1-octene. Ethylene, propylene, and 1-butene are preferable among these examples. These examples of the non-conjugated olefin may be used either solely or in combination of two or more types. An "olefin" represents an aliphatic unsaturated hydrocarbon compound having at least one carbon-carbon double bond.

[0029] Our multiblock copolymer can be manufactured by, for example, a first manufacturing method or a second manufacturing method described below.

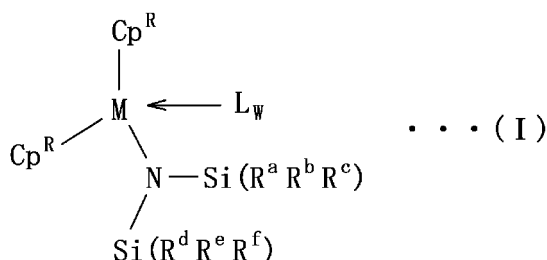
[First method for manufacturing multiblock copolymer]

[0030] A first method for manufacturing our multiblock copolymer characteristically includes copolymerizing a conjugated diene compound with a non-conjugated olefin under the presence of any of first to third polymerization catalyst compositions or a polymerization catalyst. Any polymerization method such as solution polymerization, suspension polymerization, liquid-phase bulk polymerization, emulsion polymerization, vapor-phase polymerization, or solid-phase polymerization can be used as a copolymerization method in the first method for manufacturing our multiblock copolymer. Any solvent can be used when a solvent is to be used in the copolymerization reaction as long as the solvent is inactive in the copolymerization reaction. Examples of such a solvent as described above include toluene, hexane, cyclohexane, and a mixture thereof.

< First polymerization catalyst composition >

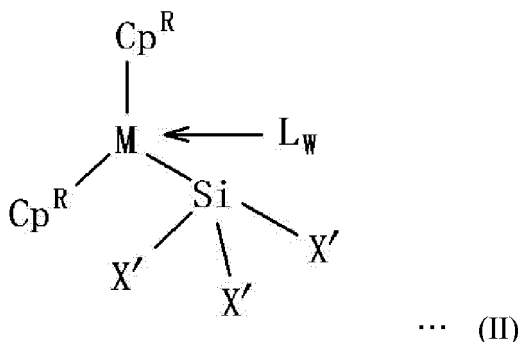
[0031] A first polymerization catalyst composition is a polymerization catalyst composition containing at least one type of complex selected from the group consisting of:

a metallocene complex represented by following general formula (I)



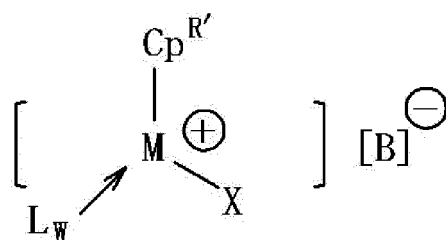
(In formula (I), M represents lanthanoid, scandium or yttrium; Cp^Rs each independently represent unsubstituted/substituted indenyl; R^a to R^f each independently represent a C₁₋₃ alkyl group or hydrogen atom; L represents a neutral Lewis base; and w represents an integer in the range of 0 to 3);

a metallocene complex represented by following general formula (II)



(In formula (II), M represents lanthanoid, scandium or yttrium; Cp^Rs each independently represent unsubstituted/substituted indenyl; X' represents hydrogen atom, halogen atom, alkoxide, thiolate, amide, silyl, or a C₁₋₂₀ hydrocarbon group; L represents a neutral Lewis base; and w represents an integer in the range of 0 to 3); and

a half metallocene cation complex represented by following general formula (III)



... (III)

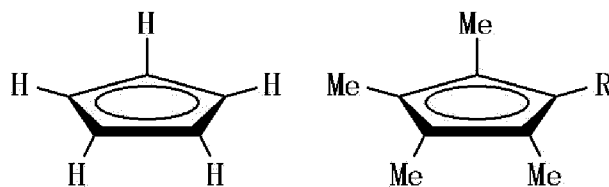
(In formula (III), M represents a lanthanoid element, scandium or yttrium; $\text{Cp}^{\text{R}'}$ represents unsubstituted/substituted cyclopentadienyl, indenyl or fluorenyl; X' represents hydrogen atom, halogen atom, alkoxide, thiolate, amide, silyl, or a C_{1-20} hydrocarbon group; L represents a neutral Lewis base; and w represents an integer in the range of 0 to 3); and $[\text{B}]^-$ represents a non-coordinating anion).

[0032] The first polymerization catalyst composition may further include other components included in a conventional metallocene complex-containing polymer catalyst composition, e.g. a promoter. In the present disclosure, a "metallocene complex" represents a complex compound in which at least one cyclopentadienyl or derivative thereof is bonded to a core metal. In this connection, a metallocene complex in which only a single cyclopentadienyl or derivative thereof is bonded to a core metal may occasionally be referred to as a "half metallocene complex" in particular.

[0033] The concentration of the complex contained in the first polymerization catalyst composition is preferably in the range of 0.1 mol/L to 0.0001 mol/L in the polymerization reaction system.

[0034] Cp^{R} s are unsubstituted/substituted indenyls in the metallocene complexes represented by general formula (I) and general formula (II). Cp^{R} having an indenyl ring as the base skeleton may be represented as $\text{C}_9\text{H}_{7-X}\text{R}_x$ or $\text{C}_9\text{H}_{11-X}\text{R}_x$, wherein X is an integer in the range of 0 to 7 or 0 to 11; Rs preferably each represent hydrocarbyl or metalloid group; and the number of carbon atoms of the hydrocarbyl group is preferably in the range of 1 to 20, more preferably in the range of 1 to 10, and further more preferably in the range of 1 to 8. Specifically, preferable examples of the hydrocarbyl group include methyl, ethyl, phenyl, benzyl groups and the like. Examples of metalloid of the metalloid group include germlyl Ge, stannyl Sn, and silyl Si. The metalloid group preferably includes a hydrocarbyl group which is defined in the same manner as the aforementioned hydrocarbyl group. Specific examples of the metalloid group include trimethylsilyl and the like. Specific examples of the substituted indenyl include 2-phenylindenyl, 2-methylindenyl, and the like. Cp^{R} s in general formula (I) and general formula (II) may be of either the same type or different types.

[0035] $\text{Cp}^{\text{R}'}$ is unsubstituted/substituted cyclopentadienyl, indenyl, fluorenyl group in the half metallocene cation complex represented by general formula (III). Unsubstituted/substituted indenyl group is preferable as $\text{Cp}^{\text{R}'}$ among these examples. $\text{Cp}^{\text{R}'}$ having a cyclopentadienyl ring as the base skeleton is represented as $\text{C}_5\text{H}_{5-X}\text{R}_x$, wherein X is an integer in the range of 0 to 5; Rs preferably each independently represent hydrocarbyl or metalloid group; and the number of carbon atoms of the hydrocarbyl group is preferably in the range of 1 to 20, more preferably in the range of 1 to 10, and further more preferably in the range of 1 to 8. Specifically, preferable examples of the hydrocarbyl group include methyl, ethyl, phenyl, benzyl groups and the like. Examples of metalloid of the metalloid group include germlyl Ge, stannyl Sn, and silyl Si. The metalloid group preferably includes a hydrocarbyl group which is defined in the same manner as the aforementioned hydrocarbyl group. Specific examples of the metalloid group include trimethylsilyl and the like. Specific examples of $\text{Cp}^{\text{R}'}$ having a cyclopentadienyl ring as the base skeleton include compounds represented by the following structural formulae:



[0036] (In these structural formulae, R represents hydrogen atom, methyl or ethyl group.)

[0037] $\text{Cp}^{\text{R}'}$ having an indenyl ring as the base skeleton, as well as preferable examples thereof, in general formula (III) is defined in the same manner as Cp^{R} in general formula (I).

[0038] $\text{Cp}^{\text{R}'}$ having a fluorenyl ring as the base skeleton in general formula (III) is represented as $\text{C}_{13}\text{H}_{9-X}\text{R}_x$ or $\text{C}_{13}\text{H}_{17-X}\text{R}_x$, wherein X is an integer in the range of 0 to 9 or 0 to 17; Rs preferably each independently represent hydrocarbyl or metalloid group; and the number of carbon atoms of the hydrocarbyl group is preferably in the range of

1 to 20, more preferably in the range of 1 to 10, and further more preferably in the range of 1 to 8. Specifically, preferable examples of the hydrocarbonyl group include methyl, ethyl, phenyl, benzyl groups and the like. Examples of metalloids of the metalloid group include germyl Ge, stannyl Sn, and silyl Si. The metalloid group preferably includes a hydrocarbonyl group which is defined in the same manner as the aforementioned hydrocarbonyl group. Specific examples of the metalloid group include trimethylsilyl and the like.

[0039] The core metal M in each of general formulae (I), (II) and (III) is a lanthanoid element, scandium or yttrium. The lanthanoid elements include fifteen elements having atomic numbers 57-71 in the periodic table and any of these elements is acceptable. Preferable examples of the core metal M include samarium Sm, neodymium Nd, praseodymium Pr, gadolinium Gd, cerium Ce, holmium Ho, scandium Sc, and yttrium Y.

[0040] The metallocene complex represented by general formula (I) includes a silylamide ligand $[-N(SiR_3)_2]$. R groups included in the silylamide ligand (i.e. R^a to R^f in general formula (I)) each independently represent a C_{1-3} alkyl group or a hydrogen atom. It is preferable that at least one of R^a to R^f is a hydrogen atom. The catalyst can be easily synthesized and a non-conjugated olefin is easily introduced due to relatively little hindrance around the silicon atom when at least one of R^a to R^f is a hydrogen atom. For similar reasons, it is more preferable that at least one of R^a to R^c is a hydrogen atom and at least one of R^d to R^f is a hydrogen atom. Methyl group is preferable as the alkyl group.

[0041] The metallocene complex represented by general formula (II) includes a silyl ligand $[-SiX'_3]$. X' groups included in the silyl ligand $[-SiX'_3]$, as well as preferable examples thereof, are defined in the same manner as X group in general formula (III) described below.

[0042] In general formula (III), X is a group selected from the group consisting of hydrogen atom, halogen atom, alkoxide, thiolate, amide, silyl, and a C_{1-20} hydrocarbon groups. Examples of the alkoxide group include: aliphatic alkoxy group such as methoxy, ethoxy, propoxy, n-butoxy, isobutoxy, sec-butoxy, tert-butoxy, and the like; and aryloxy group such as phenoxy, 2,6-di-tert-butylphenoxy, 2,6-diisopropylphenoxy, 2,6-dineopentylphenoxy, 2-tert-butyl-6-isopropylphenoxy, 2-tert-butyl-6-neopentylphenoxy, 2-isopropyl-6-neopentylphenoxy, and the like. 2,6-di-tert-butylphenoxy is preferable as the alkoxide group among these examples.

[0043] Examples of the thiolate group represented by X in general formula (III) include: aliphatic thiolate group such as thiomethoxy, thioethoxy, thiopropoxy, n-thiobutoxy, thioisobutoxy, sec-thiobutoxy, tert-thiobutoxy, and the like; and arylthiolate group such as thiophenoxy, 2,6-di-tert-butylthiophenoxy, 2,6-diisopropylthiophenoxy, 2,6-dineopentylthiophenoxy, 2-tert-butyl-6-isopropylthiophenoxy, 2-tert-butyl-6-thioneopentylphenoxy, 2-isopropyl-6-thioneopentylphenoxy, 2,4,6-triisopropylthiophenoxy, and the like. 2,4,6-triisopropylthiophenoxy is preferable as the thiolate group among these examples.

[0044] Examples of the amide group represented by X in general formula (III) include: aliphatic amide group such as dimethylamide, diethylamide, diisopropylamide, and the like; arylamide group such as phenylamide, 2,6-di-tert-butylphenylamide, 2,6-diisopropylphenylamide, 2,6-dineopentylphenylamide, 2-tert-butyl-6-isopropylphenylamide, 2-tert-butyl-6-neopentylphenylamide, 2-isopropyl-6-neopentylphenylamide, 2,4,6-tri-tert-butylphenylamide, and the like; and bis(trialkylsilyl)amide such as bis(trimethylsilyl)amide and the like. Bis(trimethylsilyl)amide is preferable as the amide group among these examples.

[0045] Examples of the silyl group represented by X in general formula (III) include trimethylsilyl, tris(trimethylsilyl)silyl, bis(trimethylsilyl)methylsilyl, trimethylsilyl(dimethyl)silyl, (triisopropylsilyl)bis(trimethylsilyl)silyl, and the like. Tris(trimethylsilyl)silyl is preferable as the silyl group among these examples.

[0046] Acceptable examples of the halogen atom represented by X in general formula (III) include fluorine, chlorine, bromine and iodine atoms. Chlorine or bromine atom is preferable. Specific examples of the C_{1-20} hydrocarbon group represented by X in general formula (III) include: normal/branched aliphatic hydrocarbon group such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, neopentyl, hexyl, octyl; aromatic hydrocarbon group such as phenyl, tolyl, naphthyl; aralkyl group such as benzyl; a hydrocarbon group containing silicon atom such as trimethylsilylmethyl, bis(trimethylsilyl)methyl; and the like. Methyl, ethyl, isopropyl, trimethylsilylmethyl, and the like are preferable as the C_{1-20} hydrocarbon group among these examples.

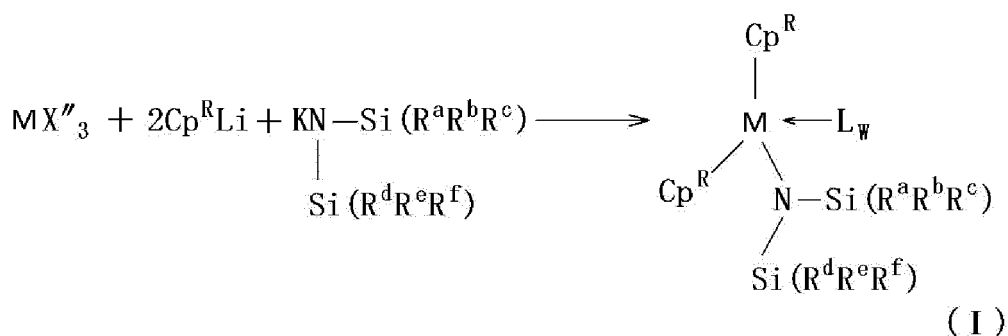
[0047] Bistrimethylsilylamide or a C_{1-20} hydrocarbon group is preferable as X in general formula (III).

[0048] Examples of the non-coordinating anion represented by $[B]^-$ in general formula (III) include quadrivalent boron anion. Specific examples of the quadrivalent boron anion include tetraphenylborate, tetrakis(monofluorophenyl)borate, tetrakis(difluorophenyl)borate, tetrakis(trifluorophenyl)borate, tetrakis(tetrafluorophenyl)borate, tetrakis(pentafluorophenyl)borate, tetrakis(tetrafluoromethylphenyl)borate, tetra(tolyl)borate, tetra(xylyl)borate, triphenyl(pentafluorophenyl)borate, [tris(pentafluorophenyl)phenyl]borate, tridecahydride-7,8-dicarbaundecaborate, and the like. Tetrakis(pentafluorophenyl)borate is preferable as the quadrivalent boron anion among these examples.

[0049] The metallocene complexes represented by general formulae (I) and (II) and the half metallocene cation complex represented by general formula (III) each further include 0 to 3, preferably 0 to 1, neutral Lewis base L. Examples of the neutral Lewis base L include tetrahydrofuran, diethyl ether, dimethylaniline, trimethylphosphine, lithium chloride, neutral olefin, neutral diolefin, and the like. The neutral Lewis bases L may be of either the same type or different types when the complex includes a plurality of neutral Lewis bases L.

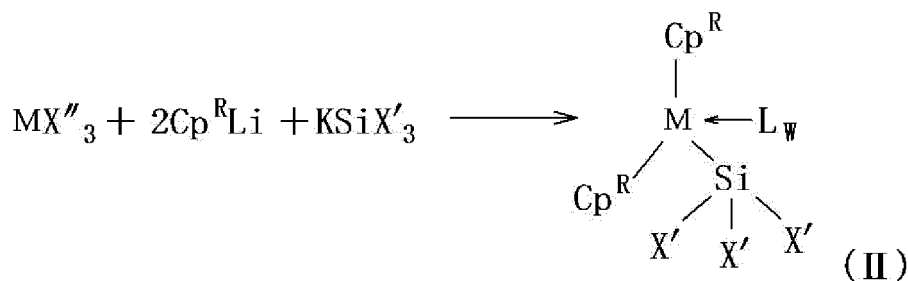
[0050] The metallocene complexes represented by general formulae (I) and (II) and the half metallocene cation complex represented by general formula (III) may each exist as any of monomer, dimer or another type of multimer.

[0051] The metallocene complex represented by general formulae (I) can be obtained by, for example, reacting lanthanoid trishalide, scandium trishalide or yttrium trishalide with an indenyl salt (such as potassium or lithium indenyl salt) and a bis(trialkylsilyl)amide salt (such as potassium or lithium salt of bis(trialkylsilyl)amide) in a solvent. The reaction temperature may be set around the room temperature, which allows production in a mild condition. The reaction time may be set as desired and is generally in the range of a few hours to a few days. Type of the reaction solvent is not particularly limited but preferably a solvent capable of dissolving the raw materials and a reaction product. For example, toluene can be used. An example of a reaction for obtaining the metallocene complex represented by general formula (I) is shown below.



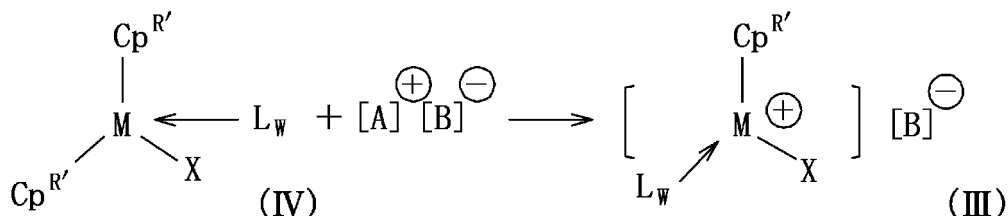
[0052] (In the reaction example above, X'' represents a halide.)

[0053] The metallocene complex represented by general formulae (II) can be obtained by, for example, reacting lanthanoid trishalide, scandium trishalide or yttrium trishalide with an indenyl salt (such as potassium or lithium indenyl salt) and a silyl salt (such as potassium or lithium silyl salt) in a solvent. The reaction temperature may be set around the room temperature, which allows production in a mild condition. The reaction time may be set as desired and is generally in the range of a few hours to a few days. Type of the reaction solvent is not particularly limited but preferably a solvent capable of dissolving the raw materials and a reaction product. For example, toluene can be used. An example of a reaction for obtaining the metallocene complex represented by general formula (II) is shown below.



[0054] (In the reaction example above, X'' represents a halide.)

[0055] The half metallocene cation complex represented by general formulae (III) can be obtained, for example, by a reaction shown below.



[0056] In the compound represented by general formula (IV), M represents a lanthanoid element, scandium or yttrium; Cp^{R'} each independently represent unsubstituted/substituted cyclopentadienyl, indenyl or fluorenyl; and X represents hydrogen atom, halogen atom, alkoxide, thiolate, amide, silyl, or a C₁₋₂₀ hydrocarbon group. L represents a neutral Lewis base and w represents an integer in the range of 0 to 3. [A]⁺ represents a cation and [B]⁻ represents a non-coordinating

anion in an ionic compound represented by $[A]^+ [B]^-$.

[0057] Examples of the cation represented by $[A]^+$ include carbonium cation, oxonium cation, amine cation, phosphonium cation, cycloheptatrienyl cation, ferrocenium cation having transition metal, and the like. Examples of the carbonium cation include trisubstituted carbonium cation such as triphenylcarbonium cation, tri(substituted phenyl)carbonium cation, and the like. Specific examples of the tri(substituted phenyl)carbonium cation include tri(methylphenyl)carbonium cation. Examples of the amine cation include: trialkylammonium cation such as trimethylammonium cation, triethylammonium cation, tripropylammonium cation, tributylammonium cation; N,N-dialkylanilinium cation such as N,N-dimethylanilinium cation, N,N-diethylanilinium cation, N,N-2,4,6-pentamethylanilinium cation; and dialkylammonium cation such as diisopropylammonium cation, dicyclohexylammonium cation; and the like. Examples of phosphonium cation include triarylphosphonium cation such as triphenylphosphonium cation, tri(methylphenyl)phosphonium cation, tri(dimethylphenyl)phosphonium cation, and the like. N,N-dialkylanilinium cation or carbonium cation is preferable and N,N-dialkylanilinium cation is particularly preferable as $[A]^+$ among these examples.

[0058] The ionic compound represented by general formula $[A]^+ [B]^-$ for use in the aforementioned reaction is, for example, a compound obtained by combining a non-coordinating anion and a cation respectively selected from the aforementioned examples and preferably N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate, triphenylcarbonium tetrakis(pentafluorophenyl)borate, and the like. The ionic compound represented by general formula $[A]^+ [B]^-$ is added to the compound represented by general formula (IV) by an amount preferably 0.1 to 10 times in mole ratio, more preferably approximately 1 times in mole ratio, as much as the amount of the compound represented by general formula (IV). In the case where the half metallocene cation complex represented by general formula (III) is used for a polymerization reaction, the half metallocene cation complex represented by general formula (III) may be directly provided into a polymerization reaction system or, alternatively, the half metallocene cation complex represented by general formula (III) may be formed in a polymerization reaction system by providing a compound represented by general formula (IV) and the ionic compound represented by general formula $[A]^+ [B]^-$ for use in the aforementioned reaction, separately, in the polymerization reaction system. Further alternatively, the half metallocene cation complex represented by general formula (III) may be formed in a polymerization reaction system by using the metallocene complex represented by general formula (I) or general formula (II) and the ionic compound represented by general formula $[A]^+ [B]^-$ for use in the aforementioned reaction in a combined manner in the polymerization reaction system.

[0059] Structures of the metallocene complex represented by general formula (I) or general formula (II) and the half metallocene cation complex represented by general formula (III) are each preferably determined through x-ray structural analysis.

[0060] The prompter applicable to the first polymerization catalyst composition can be selected according to necessity from components used as prompters in a conventional polymerization catalyst composition containing a metallocene complex. Preferable examples of the prompter include aluminoxane, an organic aluminum compound, the ionic compounds described above, and the like. Either a single type or combination of two or more types of these examples may be used as the prompter.

[0061] The aforementioned aluminoxane is preferably alkylaluminoxane and examples thereof include methylaluminoxane (MAO), modified methylaluminoxane, and the like. "MMAO-3A", manufactured by Tosoh Finechem Corporation, or the like is preferable as the modified methylaluminoxane. Provided that "Al/M" represents an element ratio of the aluminum element Al of the aluminoxane with respect to the core metal M of the metallocene complex represented by general formula (I)/(II) or the half metallocene cation complex represented by general formula (III), the content of the aluminoxane in the first polymerization catalyst composition is set such that the element ratio Al/M is in the range of 10 to 1000 approximately, preferably around 100.

[0062] On the other hand, the aforementioned organic aluminum compound is preferably an organic aluminum compound represented by general formula $AIRR'R''$ (in the formula, R and R' each independently represent a C_{1-10} hydrocarbon group or a hydrogen atom and R'' represents a C_{1-10} hydrocarbon group). Examples of the organic aluminum compound include trialkylaluminum, dialkylaluminum chloride, alkylaluminum dichloride, dialkylaluminum hydride, and the like. Trialkylaluminum is preferable as the organic aluminum compound among these examples. Examples of trialkylaluminum include triethylaluminum, triisobutylaluminum, and the like. The content of the organic aluminum compound in the first polymerization catalyst composition is preferably 1 to 50 times, more preferably around 10 times, as much as the content of the metallocene complex represented by general formula (I)/(II) or the half metallocene cation complex represented by general formula (III) when compared in mol.

[0063] Content of cis-1,4-configuration and/or the molecular weight of a resulting multiblock copolymer can be increased by using each of the metallocene complex represented by general formula (I) or general formula (II) and the half metallocene cation complex represented by general formula (III) with an appropriate prompter in combination in the first polymerization catalyst composition.

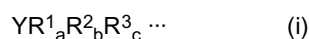
< Second polymerization catalyst composition >

[0064] Preferable examples of our polymerization catalyst composition further include another type of polymerization catalyst composition (which will be referred to as a "second polymerization catalyst composition" hereinafter). The second polymerization catalyst composition is made up of

component (A): a rare earth element compound or a reactant resulted from a reaction between the rare earth element compound and a Lewis base, wherein the rare earth element compound and the reactant thereof have no bond between a relevant rare earth metal and a carbon atom, respectively, and

component (B): at least one type of compound selected from the group consisting of (B-1) an ionic compound constituted of a non-coordinating anion and a cation, (B-2) aluminoxane, and (B-3) at least one type of halogen compound selected from a Lewis acid, a complex compound of a metal halide and a Lewis base, and an organic compound containing an active halogen.

[0065] In a case where the second polymerization catalyst composition includes at least one of the ionic compound (B-1) and the halogen compound (B-3), the second polymerization catalyst composition further includes component (C) which is an organic metal compound represented by the following formula (i):



[0066] (In formula (i), Y represents a metal selected from the group 1, 2, 12 and 13 elements in the periodic table, R¹ and R² each represent a C₁₋₁₀ hydrocarbon group or a hydrogen atom and may be of either the same type or different types, R³ represents a C₁₋₁₀ hydrocarbon group and may be of either the same type as or a different type from R¹ and R², a = 1 and b = c = 0 when Y is a metal selected from the group 1 elements in the periodic table, a = b = 1 and c = 0 when Y is a metal selected from the groups 2, 12 elements in the periodic table, and a = b = c = 1 when Y is a metal selected from the group 13 elements in the periodic table.)

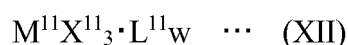
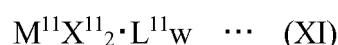
[0067] The ionic compound (B-1) and the halogen compound (B-3) need the component (C) serving as a carbon donor to the component (A) because neither the ionic compound (B-1) nor the halogen compound (B-3) has a carbon atom which can be supplied to the component (A). The second polymerization catalyst composition may include the component (C) in a case where the catalyst composition includes the aluminoxane (B-2). Further, the second polymerization catalyst composition may include other components included in a conventional rare-earth element compound-based polymer catalyst composition, e.g. a promoter. Content of the component (A) contained in the second polymerization catalyst composition is preferably in the range of 0.1 mol/l to 0.0001 mol/l in the polymerization reaction system.

[0068] The component (A) for use in the second polymerization catalyst composition is a rare earth element compound or a reactant resulted from a reaction between the rare earth element compound and a Lewis base, wherein the rare earth element compound and the reactant thereof have no bond between a relevant rare earth metal and a carbon atom, respectively. A rare earth element compound or a reactant resulted from a reaction between the rare earth element compound and a Lewis base, having no bond between a relevant rare earth metal and a carbon atom, is stable as a compound and easy to handle. In the present disclosure, a "rare earth element compound" represents a compound containing: one of lanthanoid elements constituted of atomic number 57-71 elements in the periodic table; or scandium or yttrium.

Specific examples of the lanthanoid elements include lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium.

Either a single type or combination of two or more types of the aforementioned examples may be used as the compound (A).

[0069] The rare earth element compound described above is preferably a salt or a complex compound containing a divalent/trivalent rare earth metal and more preferably a rare earth element compound having at least one type of ligand selected from hydrogen atom, halogen atom, and an organic compound residue. Further, the rare earth element compound or the reactant resulted from a reaction between the rare earth element compound and a Lewis base is represented by following general formula (XI) or general formula (XII):



[0070] (In these formulae, M¹¹ represents a lanthanoid element, scandium or yttrium, X¹¹s each independently represent hydrogen atom, halogen atom, alkoxide group, thiolate group, amide group, silyl group, aldehyde residue, ketone

residue, carboxylic residue, thiocarboxylic residue or phosphorus compound residue, L¹¹ represents a Lewis base, and w represents an integer in the range of 0 to 3.)

[0071] Specific examples of a group (ligand) bonded to a rare earth element of the rare earth element compound include: hydrogen atom; aliphatic alkoxy group such as methoxy, ethoxy, propoxy, n-butoxy, isobutoxy, sec-butoxy, tert-butoxy, and the like; phenoxy, 2,6-di-tert-butylphenoxy, 2,6-diisopropylphenoxy, 2,6-dineopentylphenoxy, 2-tert-butyl-6-isopropylphenoxy, 2-tert-butyl-6-neopentylphenoxy, 2-isopropyl-6-neopentylphenoxy; aliphatic thiolate group such as thiomethoxy, thioethoxy, thiopropoxy, thio-n-butoxy, thioisobutoxy, thio-sec-butoxy, thio-tert-butoxy, and the like; aryl thiolate group such as thiophenoxy, 2,6-di-tert-butylthiophenoxy, 2,6-diisopropylthiophenoxy, 2,6-dineopentylthiophenoxy, 2-tert-butyl-6-isopropylthiophenoxy, 2-tert-butyl-6-thioneopentylphenoxy, 2-isopropyl-6-thioneopentylphenoxy, 2,4,6-triisopropylthiophenoxy, and the like; aliphatic amide group such as dimethylamide, diethylamide, diisopropylamide, and the like; arylamide such as phenylamide, 2,6-di-tert-butylphenylamide, 2,6-diisopropylphenylamide, 2,6-dineopentylphenylamide, 2-tert-butyl-6-isopropylphenylamide, 2-tert-butyl-6-neopentylphenylamide, 2-isopropyl-6-neopentylphenylamide, 2,4,6-tert-butylphenylamide, and the like; bistralkylsilylamide such as bistrimethylsilylamide; silyl group such as trimethylsilyl, tris(trimethylsilyl)silyl, bis(trimethylsilyl)methylsilyl, trimethylsilyl(dimethyl)silyl, triisopropylsilyl(bistrimethylsilyl)silyl, and the like; a halogen atom such as fluorine, chlorine, bromine, iodine atoms; and the like. Specific examples of the ligand further include: aldehyde residue such as salicylaldehyde, 2-hydroxy-1-naphthaldehyde, 2-hydroxy-3-naphthaldehyde, and the like; a residue of hydroxyphenone such as 2'-hydroxyacetophenone, 2'-hydroxybutylphenone, 2'-hydroxypropylphenone, and the like; a residue of diketone such as acetylacetone, benzoylacetone, propionylacetone, isobutylacetone, valeryl acetone, ethylacetylacetone, and the like; a residue of carboxylic acid such as isovaleric acid, caprylic acid, octanoic acid, lauric acid, myristic acid, palmitic acid, stearic acid, isostearic acid, oleic acid, linoleic acid, cyclopentanecarboxylic acid, naphthenic acid, ethylhexanoic acid, pivalic acid, versatic acid (a product manufactured by Shell Chemicals, which is a synthetic acid composed of a mixture of isomers of C₁₀ monocarboxylic acid), phenylacetic acid, benzoic acid, 2-naphthoic acid, maleic acid, succinic acid, and the like; a residue of thocarboxylic acid such as hexanethioic acid, 2,2-dimethylbutanethioic acid, decanethioic acid, thiobenzoic acid, and the like; a residue of phosphate ester such as dibutyl phosphate, dipentyl phosphate, dihexyl phosphate, diheptyl phosphate, dioctyl phosphate, bis(2-ethylhexyl) phosphate, bis(1-methylheptyl) phosphate, dilauryl phosphate, dioleoyl phosphate, diphenyl phosphate, bis(p-nonylphenyl) phosphate, bis(polyethylene glycol-p-nonylphenyl) phosphate, (butyl)(2-ethylhexyl) phosphate, (1-methylheptyl)(2-ethylhexyl) phosphate, (2-ethylhexyl)(p-nonylphenyl) phosphate, and the like; a residue of phosphonic ester such as monobutyl (2-ethylhexyl)phosphite, mono-2-ethylhexyl (2-ethylhexyl)phosphite, mono-2-ethylhexyl phenylphosphite, mono-p-nonylphenyl (2-ethylhexyl)phosphite, mono-2-ethylhexyl phosphite, mono-1-methylheptyl phosphite, mono-p-nonylphenyl phosphite, and the like; a residue of phosphinic acid such as dibutyl phosphinic acid, bis(2-ethylhexyl)phosphinic acid, bis(1-methylheptyl)phosphinic acid, dilauryl phosphinic acid, dioleoyl phosphinic acid, diphenyl phosphinic acid, bis(p-nonylphenyl)phosphinic acid, butyl(2-ethylhexyl)phosphinic acid, (2-ethylhexyl)(1-methylheptyl)phosphinic acid, (2-ethylhexyl)(p-nonylphenyl)phosphinic acid, butyl phosphinic acid, 2-ethylhexyl phosphinic acid, 1-methylheptyl phosphinic acid, oleoyl phosphinic acid, lauryl phosphinic acid, phenyl phosphinic acid, p-nonylphenyl phosphinic acid, and the like. Either a single type or combination of two or more types of the aforementioned examples or the like may be used as the ligands.

[0072] In the component (A) for use in the second polymerization catalyst composition, examples of the Lewis base to be reacted with the rare earth element compound include tetrahydrofuran, diethyl ether, dimethylaniline, trimethylphosphine, lithium chloride, neutral olefins, neutral diolefins, and the like. In this connection, in a case where the rare earth element compound is reacted with a plurality of Lewis bases (i.e. in a case where w = 2 or 3 in formula (XI) and formula (XII)), these Lewis bases L¹¹s may be of either the same type or the different types.

[0073] The component (B) for use in the second polymerization catalyst composition is at least one type of compound selected from the group consisting of: an ionic compound (B-1); aluminoxane (B-2); and a halogen compound (B-3). The total content of the component (B) in the second polymerization catalyst composition is preferably 0.1 to 50 times as much as the content of the component (A) in the composition when compared in mol.

[0074] The ionic compound, referred to as (B-1) in the present disclosure, is constituted of a non-coordinating anion and a cation. Examples of the ionic compound (B-1) include an ionic compound capable of being reacted with the compound (A), i.e. a rare earth element compound or a reactant resulted from a reaction between the rare earth element compound and a Lewis base, to generate a cationic transition metal compound. In this connection, examples of the non-coordinating anion include tetraphenylborate, tetrakis(monofluorophenyl)borate, tetrakis(difluorophenyl)borate, tetrakis(trifluorophenyl)borate, tetrakis(tetrafluorophenyl)borate, tetrakis(pentafluorophenyl)borate, tetrakis(tetrafluoromethylphenyl)borate, tetra(tolyl)borate, tetra(xylyl)borate, triphenyl(pentafluorophenyl)borate, [tris(pentafluorophenyl)](phenyl)borate, tridecahydride-7,8-dicarbaundecaborate, and the like. Examples of the cation include carbonium cation, oxonium cation, ammonium cation, phosphonium cation, cycloheptatrienyl cation, ferrocium cation having transition metal, and the like. Specific examples of carbonium cation include trisubstituted carbonium cation such as triphenylcarbonium cation, tri(substituted phenyl)carbonium cation, and the like. Specific examples of the tri(substituted phenyl)carbonium cation include tri(methylphenyl)carbonium cation, tri(dimethylphenyl)carbonium cation, and the like. Spe-

cific examples of the ammonium cation include: trialkylammonium cation such as trimethylammonium cation, triethylammonium cation, tripropylammonium cation, tributylammonium cation (e.g. tri(n-butyl)ammonium cation); N,N-dialkylanilinium cation such as N,N-dimethylanilinium cation, N,N-diethylanilinium cation, N,N-2,4,6-pentamethylanilinium cation, and the like; and dialkylammonium cation such as diisopropylammonium cation, dicyclohexylammonium cation, and the like. Specific examples of phosphonium cation include triarylphosphonium cation such as triphenylphosphonium cation, tri(methylphenyl)phosphonium cation, tri(dimethylphenyl)phosphonium cation, and the like. A compound as a combination of a non-coordinating anion and a cation selected from the aforementioned examples, respectively, is preferably used as the ionic compound (B-1). Specific examples of the ionic compound (B-1) include N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate, triphenylcarbonium tetrakis(pentafluorophenyl)borate, and the like. Either a single type or combination of two or more types of the aforementioned examples may be used as the ionic compound (B-1). The content of the ionic component (B-1) in the second polymerization catalyst composition is preferably 0.1 to 10 times, more preferably approximately 1 times, as much as the content of the component (A) when compared in mol.

[0075] Aluminoxane, referred to as (B-2) in the present disclosure, is a compound obtained by bringing an organic aluminum compound into contact with a condensing agent. Examples of aluminoxane include a chain aluminoxane or a cyclic aluminoxane represented by general formula: $(-Al(R')O-)$ and having repeating units (in the formula, R' represents a C_{1-10} hydrocarbon group; some of the hydrocarbon groups may be substituted with halogen atom and/or alkoxy group; and polymerization degree of the repeating units is preferably ≥ 5 and more preferably ≥ 10). Specific examples of R' include methyl, ethyl, propyl, isobutyl groups and the like. Methyl group is preferable as R' among these examples. Examples of the organic aluminum compound used as a raw material of aluminoxane include trialkylaluminum such as trimethylaluminum, triethylaluminum, triisobutylaluminum, and a mixture thereof. Trimethylaluminum is particularly preferable among these examples as the organic aluminum compound. An aluminoxane obtained by using a mixture of trimethylaluminum and tributylaluminum as the raw material can be suitably used, for example. Provided that "Al/M" represents an element ratio of the aluminum element Al of aluminoxane with respect to the rare earth element M constituting the component (A), the content of aluminoxane (B-2) in the second polymerization catalyst composition is preferably set such that the element ratio Al/M is in the range of 10 to 1000 approximately.

[0076] The halogen compound, referred to as (B-3) in the present disclosure, is at least one type of halogen compound selected from a Lewis acid, a complex compound of a metal halide and a Lewis base, and an organic compound containing an active halogen. The halogen compound (B-3) is, for example, capable of being reacted with the component (A), i.e. a rare earth element compound or a reactant resulted from a reaction between the rare earth element compound and a Lewis base, to generate a cationic transition metal compound. The total content of the halogen compound (B-3) in the second polymerization catalyst composition is preferably 1 to 5 times as much as the content of the component (A) when compared in mol.

[0077] Examples of the Lewis acid include a boron-containing halogen compound such as $B(C_6F_5)_3$, an aluminum-containing halogen compound such as $Al(C_6F_5)_3$, and a halogen compound containing a group III, IV, V, VI or VIII element in the periodic table. Preferable examples of the Lewis acid include aluminum halide and organic metal halide. Chlorine or bromine is preferable as the halogen element. Specific examples of the Lewis acid include methylaluminum dibromide, methylaluminum dichloride, ethylaluminum dibromide, ethylaluminum dichloride, butylaluminum dibromide, butylaluminum dichloride, dimethylaluminum bromide, dimethylaluminum chloride, diethylaluminum bromide, diethylaluminum chloride, dibutylaluminum bromide, dibutylaluminum chloride, methylaluminum sesquibromide, methylaluminum sesquichloride, ethylaluminum sesquibromide, ethylaluminum sesquichloride, dibutyltin dichloride, aluminum tribromide, antimony trichloride, antimony pentachloride, phosphorus trichloride, phosphorus pentachloride, tin tetrachloride, titanium tetrachloride, tungsten hexachloride, and the like. Diethylaluminum chloride, ethylaluminum sesquichloride, ethylaluminum dichloride, diethylaluminum bromide, ethylaluminum sesquibromide, and ethylaluminum dibromide are particularly preferable as the Lewis acid among these examples.

[0078] Examples of the metal halide which, together with a Lewis base, constitutes a complex compound include beryllium chloride, beryllium bromide, beryllium iodide, magnesium chloride, magnesium bromide, magnesium iodide, calcium chloride, calcium bromide, calcium iodide, barium chloride, barium bromide, barium iodide, zinc chloride, zinc bromide, zinc iodide, cadmium chloride, cadmium bromide, cadmium iodide, mercury chloride, mercury bromide, mercury iodide, manganese chloride, manganese bromide, manganese iodide, rhenium chloride, rhenium bromide, rhenium iodide, copper chloride, copper iodide, silver chloride, silver bromide, silver iodide, gold chloride, gold iodide, gold bromide, and the like. Magnesium chloride, calcium chloride, barium chloride, manganese chloride, zinc chloride, copper chloride are preferable as the metal halide among these examples. Magnesium chloride, manganese chloride, zinc chloride, copper chloride are particularly preferable.

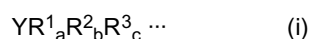
[0079] Further, preferable examples of the Lewis base constituting, together with the metal halide, a complex compound include a phosphorus compound, a carbonyl compound, a nitrogen compound, an ether compound, alcohol, and the like. Specifically, acceptable examples of the Lewis base include tributyl phosphate, tris (2-ethylhexyl) phosphate, triphenyl phosphate, tricresyl phosphate, triethylphosphine, tributylphosphine, triphenylphosphine, diethylphosphinoethane, diphenylphosphinoethane, acetylacetone, benzoylacetone, propionitrileacetone, valerylacetone, ethylacetylacetone,

methyl acetoacetate, ethyl acetoacetate, phenyl acetoacetate, dimethyl malonate, diethyl malonate, diphenyl malonate, acetic acid, octanoic acid, 2-ethyl-hexanoic acid, oleic acid, stearic acid, benzoic acid, naphthenic acid, versatic acid, triethylamine, N,N-dimethylacetoamide, tetrahydrofuran, diphenyl ether, 2-ethyl-hexyl alcohol, oleyl alcohol, stearyl alcohol, phenol, benzyl alcohol, 1-decanol, lauryl alcohol, and the like. Tris (2-ethylhexyl) phosphate, tricresyl phosphate, acetylacetone, 2-ethyl-hexanoic acid, versatic acid, 2-ethyl-hexyl alcohol, 1-decanol, lauryl alcohol are preferable as the Lewis base among these examples.

[0080] 0.01 to 30 mol (preferably 0.5 to 10 mol) per 1 mol of the metal halide, of the aforementioned Lewis base, is reacted with the metal halide. Metals remaining in the polymer can be reduced by using a reactant obtained by this reaction between the metal halide and the Lewis base.

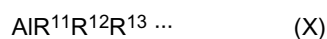
[0081] Examples of the organic compound containing active halogen, as the compound (B-3), include benzyl chloride and the like.

[0082] The component (C) for use in the second polymerization catalyst composition is an organic metal compound represented by the aforementioned formula (i):



[0083] (In formula (i), Y represents a metal selected from the group 1, 2, 12 and 13 elements in the periodic table, R¹ and R² each represent a C₁₋₁₀ hydrocarbon group or a hydrogen atom and may be of either the same type or different types, R³ represents a C₁₋₁₀ hydrocarbon group and may be of either the same type as or a different type from R¹ and R², a = 1 and b = c = 0 when Y is a metal selected from the group 1 elements in the periodic table, a = b = 1 and c = 0 when Y is a metal selected from the groups 2, 12 elements in the periodic table, and a = b = c = 1 when Y is a metal selected from the group 13 elements in the periodic table.)

[0084] The component (C) is preferably an organic aluminum compound represented by general formula (X):

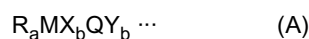


[0085] (In formula (X), R¹¹ and R¹² each represent a C₁₋₁₀ hydrocarbon group or a hydrogen atom and may be of either the same type or different types, R¹³ represents a C₁₋₁₀ hydrocarbon group and may be of either the same type as or a different type from R¹¹ and R¹².)

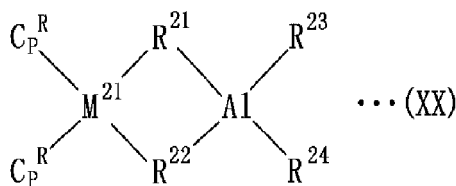
[0086] Examples of the organic aluminum compound represented by general formula (X) include trimethylaluminum, triethylaluminum, tri-n-propylaluminum, triisopropylaluminum, tri-n-butylaluminum, triisobutylaluminum, tri-t-butylaluminum, tri-pentylaluminum, trihexylaluminum, tricyclohexylaluminum, trioctylaluminum; hydrogenated diethylaluminum, hydrogenated di-n-propylaluminum, hydrogenated di-n-butylaluminum, hydrogenated diisobutylaluminum, hydrogenated dihexylaluminum, hydrogenated diisohexylaluminum, hydrogenated dioctylaluminum, hydrogenated diisooctylaluminum, ethylaluminum dihydride, n-propylaluminum dihydride, isobutylaluminum dihydride, and the like. Triethylaluminum, triisobutylaluminum, hydrogenated diethylaluminum and hydrogenated diisobutylaluminum are preferable as the organic aluminum compound among these examples. Either a single type or combination of two or more types of the aforementioned examples of the organic metal compound may be used as the compound (C). The content of the organic aluminum compound (B-3) in the second polymerization catalyst composition is preferably 1 to 50 times, more preferably approximately 10 times, as much as the content of the component (A) when compared in mol.

< Polymerization catalyst >

[0087] Preferable examples of a polymerization catalyst include a metallocene-based composite catalyst represented by the following formula (A):



[0088] (In formula (A), R_s each independently represent unsubstituted/substituted indenyl; M is coordinated with R_s; M represents a lanthanoid element, scandium or yttrium; X_s each independently represent a C₁₋₂₀ hydrocarbon group; M and Q are μ-coordinated with X; Q represents a group 13 element in the periodic table; Y_s each independently represent a C₁₋₂₀ hydrocarbon group or a hydrogen atom; Q is coordinated with Y; and a = b = 2). The aforementioned metallocene-based composite catalyst is more preferably a metallocene-based composite catalyst represented by following formula (XX):



[0089] (In formula (XX), M²¹ represents a lanthanoid element, scandium or yttrium; Cp^Rs each independently represent unsubstituted/substituted indenyl; R²¹ and R²² each independently represent a C₁₋₂₀ hydrocarbon group; M²¹ and Al are μ -coordinated with R²¹ and R²²; and R²³ and R²⁴ each independently represent a C₁₋₂₀ hydrocarbon group or a hydrogen atom.)

[0090] A "metallocene-based composite catalyst" represents a compound containing a rare earth element (lanthanoid element, scandium or yttrium) and a group 13 element in the periodic table. It is possible to reduce an amount of alkylaluminum for use in synthesis of the multiblock copolymer or even eliminate the alkylaluminum by using the metallocene-based composite catalyst described above, for example, a catalyst which has been combined with aluminum catalyst in advance to be a composite. It should be noted in this connection that a large amount of alkylaluminum is needed during synthesis of the multiblock copolymer if the conventional catalyst system is employed. For example, alkylaluminum must be used by an amount at least 10 times as much as the chemically equivalent amount of a relevant metal catalyst in the conventional catalyst system. In contrast, in the case of using the metallocene-based composite catalyst described above, a good catalytic effect is demonstrated by adding alkylaluminum by an amount around 5 times as much as the chemically equivalent amount of the metal catalyst. The expression that "M and Q are μ -coordinated with X" represents that M and Q are coordinated with X in a crosslinking manner.

[0091] With regard to the metallocene-based composite catalyst represented by formula (A) above, the metal M is a lanthanoid element, scandium or yttrium. The lanthanoid elements include the fifteen elements having atomic numbers 57-71 and any of these elements is acceptable. Preferable examples of the core metal M include samarium Sm, neodymium Nd, praseodymium Pr, gadolinium Gd, cerium Ce, holmium Ho, scandium Sc, and yttrium Y.

[0092] In formula (A), Rs each independently represent unsubstituted/substituted indenyl and M is coordinated with Rs. Specific examples of the substituted indenyl group include 1,2,3-trimethyl indenyl, heptamethylindenyl, 1,2,4,5,6,7-hexamethylindenyl, and the like.

[0093] In formula (A), Q represents a group 13 element in the periodic table and specific examples thereof include boron, aluminum, gallium, indium, thallium, and the like.

[0094] In formula (A), Xs each independently represent a C₁₋₂₀ hydrocarbon group and M and Q are μ -coordinated with X. Examples of the C₁₋₂₀ hydrocarbon group include methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, decyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, stearyl, and the like.

[0095] In formula (A), Ys each independently represent a C₁₋₂₀ hydrocarbon group or a hydrogen atom and Q is coordinated with Y. In this connection, examples of the C₁₋₂₀ hydrocarbon group include methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, decyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, stearyl, and the like.

[0096] On the other hand, in the metallocene-based composite catalyst represented by formula (XX) above, the metal M²¹ in formula (XX) is a lanthanoid element, scandium or yttrium. The lanthanoid elements include the fifteen elements having atomic numbers 57-71 and any of these elements is acceptable. Preferable examples of the core metal M²¹ include samarium Sm, neodymium Nd, praseodymium Pr, gadolinium Gd, cerium Ce, holmium Ho, scandium Sc, and yttrium Y.

[0097] In formula (XX), Cp^Rs are unsubstituted/substituted indenyls. Cp^R having an indenyl ring as the base skeleton may be represented as C₉H_{7-X}R_X or C₉H_{11-X}R_X, wherein X is an integer in the range of 0 to 7 or 0 to 11; Rs preferably each independently represent hydrocarbonyl or metalloidy group; and the number of carbon atoms of the hydrocarbonyl group is preferably in the range of 1 to 20, more preferably in the range of 1 to 10, and further more preferably in the range of 1 to 8. Specifically, preferable examples of the hydrocarbonyl group include methyl, ethyl, phenyl, benzyl groups and the like. Examples of metalloidy of the metalloidy group include germyl Ge, stannyl Sn, and silyl Si. The metalloidy group preferably includes a hydrocarbonyl group which is defined in the same manner as the aforementioned hydrocarbonyl group. Specific examples of the metalloidy group include trimethylsilyl and the like. Specific examples of the substituted indenyl include 2-phenylindenyl, 2-methylindenyl, and the like. The two Cp^Rs in general formula (XX) may be of either the same type or different types.

[0098] In formula (XX), R²¹ and R²² each independently represent a C₁₋₂₀ hydrocarbon group and M²¹ and Al are μ -coordinated with R²¹ and R²². In this connection, examples of the C₁₋₂₀ hydrocarbon group include methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, decyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, stearyl, and the like.

[0099] In formula (XX), R²³ and R²⁴ each independently represent a C₁₋₂₀ hydrocarbon group or a hydrogen atom. In

this connection, examples of the C₁₋₂₀ hydrocarbon group include methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, decyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, stearyl, and the like.

[0100] The metallocene-based composite catalyst described above can be obtained by reacting a metallocene complex represented by formula (I) described in connection with the first polymerization catalyst composition, with an organic aluminum compound represented by AlR²⁵R²⁶R²⁷ in a solvent, wherein R²⁵ and R²⁶ each independently represent a monovalent C₁₋₂₀ hydrocarbon group or a hydrogen atom; R²⁷ represents a monovalent C₁₋₂₀ hydrocarbon group; and R²⁷ may be of either the same type as or a different type from R²⁵ and R²⁶. Examples of the monovalent C₁₋₂₀ hydrocarbon group include methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, decyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, stearyl, and the like.

[0101] The reaction temperature may be set around the room temperature, which allows production in a mild condition. The reaction time may be set as desired and is generally in the range of a few hours to a few days. Type of the reaction solvent is not particularly limited but preferably a solvent capable of dissolving the raw materials and a reaction product. For example, toluene or hexane can be used. The structure of the metallocene-based composite catalyst described above is preferably determined through ¹H-NMR or x-ray structural analysis.

[0102] Specific examples of the organic aluminum compound include trimethylaluminum, triethylaluminum, tri-n-propylaluminum, triisopropylaluminum, tri-n-butylaluminum, triisobutylaluminum, tri-t-butylaluminum, tripentylaluminum, trihexylaluminum, tricyclohexylaluminum, trioctylaluminum; hydrogenated diethylaluminum, hydrogenated di-n-propylaluminum, hydrogenated di-n-butylaluminum, hydrogenated diisobutylaluminum, hydrogenated dihexylaluminum, hydrogenated diisohexylaluminum, hydrogenated dioctylaluminum, hydrogenated diisooctylaluminum; ethylaluminum dihydride, n-propylaluminum dihydride, isobutylaluminum dihydride, and the like. Triethylaluminum, triisobutylaluminum, hydrogenated diethylaluminum and hydrogenated diisobutylaluminum are preferable as the organic aluminum compound among these examples. Either a single type or combination of two or more types of these examples may be used as the organic aluminum compound. An amount of the organic aluminum compound for use in generation of the metallocene-based composite catalyst is preferably 1 to 50 times, more preferably approximately 10 times, as much as the amount of the metallocene complex when compared in mol.

< Third polymerization catalyst composition >

[0103] Preferable examples of our polymerization catalyst composition further include yet another type of polymerization catalyst composition composed of the metallocene-based composite catalyst described above and a boron anion. This polymerization catalyst composition will be referred to as a "third polymerization catalyst composition" hereinafter. The third polymerization catalyst composition may also include other components, e.g. a promoter, contained in a conventional polymerization catalyst composition containing a metallocene complex. A catalyst composed of the metallocene-based composite catalyst and a boron anion is occasionally referred to as a "two-component catalyst". It is possible to manufacture a multiblock copolymer via copolymerization of a conjugated diene compound with a non-conjugated olefin by using the third polymerization catalyst composition, as is the case with using the metallocene-based composite catalyst described above. Further, when the third polymerization catalyst composition is used, it is possible to control contents of the respective monomer components in the multiblock copolymer as desired because the third polymerization catalyst composition contains a boron anion.

[0104] Specific examples of the boron anion constituting a two-component catalyst as the third polymerization catalyst composition include a quadrivalent boron anion. Examples of the quadrivalent boron anion include tetraphenylborate, tetrakis(monofluorophenyl)borate, tetrakis(difluorophenyl)borate, tetrakis(trifluorophenyl)borate, tetrakis(tetrafluorophenyl)borate, tetrakis(pentafluorophenyl)borate, tetrakis(tetrafluoromethylphenyl)borate, tetra(tolyl)borate, tetra(xylyl)borate, triphenyl(pentafluorophenyl)borate, [tris(pentafluorophenyl)](phenyl)borate, tridecahydride-7,8-dicarbaundecaborate, and the like. Tetrakis(pentafluorophenyl)borate is preferable as the quadrivalent boron anion among these examples.

[0105] The boron anion can be used as an ionic compound in which the boron anion is combined with a cation. Examples of the cation include carbonium cation, oxonium cation, amine cation, phosphonium cation, cycloheptatrienyl cation, ferrocium cation having transition metal, and the like. Specific examples of carbonium cation include trisubstituted carbonium cation such as triphenylcarbonium cation, tri(substituted phenyl)carbonium cation, and the like. Specific examples of the tri(substituted phenyl)carbonium cation include tri(methylphenyl)carbonium cation, and the like. Specific examples of the amine cation include: trialkylammonium cation such as trimethylammonium cation, triethylammonium cation, tripropylammonium cation, tributylammonium cation; N,N-dialkylanilinium cation such as N,N-dimethylanilinium cation, N,N-diethylanilinium cation, N,N-2,4,6-pentamethylanilinium cation, and the like; and dialkylammonium cation such as diisopropylammonium cation, dicyclohexylammonium cation, and the like. Specific examples of phosphonium cation include triarylphosphonium cation such as triphenylphosphonium cation, tri(methylphenyl)phosphonium cation, tri(dimethylphenyl)phosphonium cation, and the like. N,N-dialkylanilinium cation and carbonium cation are preferable and N,N-dialkylanilinium cation is particularly preferable as the cation among these examples. Accordingly, N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate, triphenylcarbonium tetrakis(pentafluorophenyl)borate, and the like are

preferable as the ionic compound. The ionic compound composed of the boron anion and the cation is preferably added by an amount 0.1 to 10 times, more preferably approximately 1 times, as much as the amount of the metallocene-based composite catalyst when compared in mol.

[0106] It is necessary to use the metallocene-based composite catalyst and the boron anion in the third polymerization catalyst composition. However, the metallocene-based composite catalyst represented by formula (A) cannot be synthesized when a boron anion exists in a reaction system for reacting a metallocene complex represented by formula (I) with an organic aluminum compound. Accordingly, preparation of the third polymerization catalyst composition requires synthesizing the metallocene-based composite catalyst in advance, isolating and purifying the metallocene-based composite catalyst thus synthesized, and then combining the metallocene-based composite catalyst with a boron anion.

[0107] Preferable examples of the promoter which may be used for the third polymerization catalyst composition include aluminosilane and the like, as well as the aforementioned organic aluminum compound represented by $AlR^{25}R^{26}R^{27}$. Aluminosilane is defined in the same manner as described in connection with the first polymerization catalyst composition and the second polymerization catalyst composition.

[0108] In a first method for manufacturing our multiblock copolymer, polymerization may be carried out in the same manner as the conventional method for manufacturing polymer by using a coordinated ionic polymerization catalyst, except that any of the first, second, and third polymerization catalyst compositions or the polymerization catalyst described above is used in the former. When any of the aforementioned first, second, and third polymerization catalyst compositions is to be used, for example, (i) the respective components to constitute the polymer catalyst composition may be separately provided in a polymerization reaction system containing conjugated diene compound monomers and non-conjugated olefin monomers, so that the polymer catalyst composition is formed in the reaction system, or (ii) the polymer catalyst composition, which has been prepared in advance, may be provided in a polymerization reaction system. In the case of (ii) above, a metallocene complex or a half metallocene cation complex (an active species) activated by a promoter may be provided. Amounts of the metallocene complex, a half metallocene cation complex or a metallocene-based composite complex contained in the polymerization catalyst composition or the polymerization catalyst, for use, is preferably 0.0001 to 0.01 times as much as the total amount of the conjugated diene compound and the non-conjugated olefin in mol.

[0109] The copolymerization reaction can be stopped by using a polymerization terminator such as ethanol, isopropanol or the like in the first method for manufacturing our multiblock copolymer.

[0110] A copolymerization reaction of the conjugated diene compound and the non-conjugated olefin is preferably carried out in an atmosphere of inert gas, preferably in an atmosphere of nitrogen or argon in the first method for manufacturing our multiblock copolymer. The polymerization temperature in the copolymerization reaction, although it is not particularly restricted, is preferably in the range of $-100\text{ }^{\circ}\text{C}$ to $200\text{ }^{\circ}\text{C}$ and may be around the room temperature, for example. Pressure during the copolymerization reaction is preferably in the range of 0.1 MPa to 10.0 MPa in terms of capturing sufficient amounts of the conjugated diene compound and the non-conjugated olefin into the polymerization reaction system. Reaction time of the copolymerization reaction, although it is not particularly restricted, is preferably in the range of 1 second to 10 days and may be appropriately selected depending on the conditions such as types of monomers to be copolymerized, type of the catalyst, the polymerization temperature, and the like.

[0111] Regarding copolymerization of a conjugated diene compound and a non-conjugated olefin in the first method for manufacturing our multiblock copolymer, concentration (mol/L) of the conjugated diene compound and concentration (mol/L) of the non-conjugated olefin when polymerization is started preferably satisfy the formula:

concentration of non-conjugated olefin/concentration of conjugated diene compound ≥ 1.0 ,
more preferably satisfy the formula:

concentration of non-conjugated olefin/concentration of conjugated diene compound ≥ 1.3 , and
further more preferably satisfy the formula:

concentration of non-conjugated olefin/concentration of conjugated diene compound ≥ 1.7 .

[0112] A non-conjugated olefin can be efficiently introduced to a reaction mixture by setting the value of "concentration of non-conjugated olefin/concentration of conjugated diene compound" to be ≥ 1 .

[Second method for manufacturing multiblock copolymer]

[0113] It is possible to manufacture our multiblock copolymer without using any of the first, second, and third polymerization catalyst compositions or the polymerization catalyst described above but rather using a conventional coordinated ionic polymerization catalyst, by adjusting the manner of charging monomers into a polymerization reaction system. Specifically, a second method for manufacturing our multiblock copolymer controls a chain structure of a multiblock

copolymer by controlling the manner of charging a conjugated diene compound under the presence of a non-conjugated olefin, thereby successfully controlling arrangement of monomer units in the multiblock copolymer. A "polymerization reaction system" represents a site where a conjugated diene compound and a non-conjugated olefin are copolymerized and specific examples thereof include a reaction vessel and the like in the present disclosure.

5 **[0114]** A conjugated diene compound may be charged into a polymerization reaction system either continuously or non-continuously. Alternatively, continuous charging and non-continuous charging may be combined. "Continuous charging" represents adding a substance into a system at a constant feeding rate for a certain period.

10 **[0115]** It is possible to control a concentration ratio of monomers in a polymerization reaction system for copolymerizing a conjugated diene compound and a non-conjugated olefin, by non-continuously or continuously charging the conjugated diene compound into the polymerization reaction system, thereby imparting a chain structure (i.e. an arrangement of monomer units) in a resulting multiblock copolymer with a specific feature. Further, formation of homopolymers of the conjugated diene compound can be suppressed because the non-conjugated olefin exists in the polymerization reaction system when the conjugated diene compound is charged in this case. The conjugated diene compound may be charged after polymerization of the non-conjugated olefin is started, in this regard.

15 **[0116]** In a case where our multiblock copolymer is manufactured by the second manufacturing method, it is effective to continuously charge a conjugated diene compound into a polymerization reaction system where polymerization of a non-conjugated olefin has already started, i.e. under the presence of the non-conjugated olefin in such a state. In this regard, it is particularly effective to repeat, twice or more, an operation of polymerizing a non-conjugated olefin in a polymerization reaction system and then continuously charging a conjugated diene compound into the polymerization reaction system under the presence of the non-conjugated olefin in such a state.

20 **[0117]** The second manufacturing method is not particularly restricted, except that the manner of charging monomers into a polymerization reaction system is specified as described above, and may be carried out by using any polymerization method such as solution polymerization, suspension polymerization, liquid-phase bulk polymerization, emulsion polymerization, vapor-phase polymerization, or solid-phase polymerization. Further, the second manufacturing method can implement copolymerization of conjugated diene compound monomers and non-conjugated olefin monomers in the same manner as the first manufacturing method, except that the manner of charging monomers into a polymerization reaction system is specified as described above in the former.

25 **[0118]** The second manufacturing method necessitates controlling the manner of charging a conjugated diene compound into a polymerization reaction system. Specifically, it is preferable to control an amount and/or the number of charging a conjugated diene compound in this regard. Examples of a method for controlling the manner of charging a conjugated diene compound include automatic control by a computer program or the like and manual control by using a timer or the like, without being limited thereto. Further, a conjugated diene compound may be charged either continuously or non-continuously as described, without particular limitation in this regard. In a case where a conjugated diene compound is charged non-continuously, the number of charging the conjugated diene compound is not particularly restricted as long as our multiblock copolymer can be manufactured.

30 **[0119]** It is preferable that a non-conjugated olefin is continuously supplied to a polymerization reaction system in the second manufacturing method because the non-conjugated olefin must exist in the polymerization reaction system when a conjugated diene compound is charged. A method for supplying the non-conjugated olefin is not particularly restricted, otherwise.

35 **[0120]** A multiblock copolymer thus obtained by the first or second manufacturing method is subjected to, after the copolymerization reaction is stopped as required, separation from the polymerization reaction system by using, e.g. a large amount of solvent, then vacuum dry and the like for applications as desired.

40 [Rubber composition]

45 **[0121]** Components of our rubber composition are not particularly restricted as long as the rubber composition contains the aforementioned multiblock copolymer as a rubber component and may be appropriately selected according to the purpose. The rubber composition may contain various types of additives generally used for a rubber composition, such as inorganic filler, carbon black, crosslinking agent, and the like.

50 **[0122]** Types of rubber components other than the aforementioned multiblock copolymer are not particularly restricted and one or more types of rubber components can be appropriately selected according to the purpose and included in the rubber composition. Examples of other rubber components include natural rubber, various types of butadiene rubbers, various types of styrene-butadiene copolymer rubber, isoprene rubber, a bromide of isobutylene and p-methylstyrene, chloroprene rubber, ethylene-propylene copolymer rubber, ethylene-propylene-diene copolymer rubber, styrene-isoprene copolymer rubber, styrene-isoprene-butadiene copolymer rubber, isoprene-butadiene copolymer rubber, chlorosulfonated polyethylene, acrylic rubber, epichlorohydrin rubber, polysulfide rubber, silicone rubber, fluororubber, urethane rubber, and the like.

55 **[0123]** The rubber composition may contain as a reinforcing filler at least one type of filler selected from black filler

such as carbon black and white filler such as silica and an inorganic compound. Content of the reinforcing filler is not particularly restricted and may change, depending on types and compositions of the reinforcing filler and the rubber components for use in the rubber composition, and applications of the rubber composition, but is preferably 10 to 200 parts by mass and more preferably 30 to 100 parts by mass with respect to 100 parts by mass of the rubber components.

The content of the reinforcing filler ≥ 10 parts by mass ensures obtaining a required reinforcing effect in a satisfactory manner. The content of the reinforcing filler ≤ 200 parts by mass ensures good mixture of the filler and the rubber components.

[0124] Types of carbon black which can be used as black filler are not particularly limited and examples thereof include carbon blacks of SAF, ISAF, HAF (N330), FF, FEF, GPF, SRF, CF, FT and MT grades. Either a single type or combination of two or more types of these examples may be used as carbon black. These examples of carbon black may be used in combination with white filler.

[0125] Types of white filler are not particularly limited and may be selected according to the purpose. Examples of the white filler include silica and an inorganic compound represented by general formula: $mM \cdot xSiO_y \cdot zH_2O \cdots (V)$ [In the formula, M represents at least one type of substance selected from: metal selected from the group consisting of aluminum, magnesium, titanium, calcium and zirconium; oxide or hydroxide of the metal; hydrates of the oxide/hydroxide; and a carbonate salt of the metal, m, x, y and z represent an integer in the range of 1 to 5, an integer in the range of 0 to 10, an integer in the range of 2 to 5, and an integer in the range of 0 to 10, respectively.] Type of silica is not particularly restricted and examples thereof for use include wet silica, dry silica, colloidal silica, and the like. Type of the inorganic compound represented by formula (V) is not particularly restricted and examples thereof include: alumina (Al_2O_3) such as γ -alumina, α -alumina; alumina monohydrate ($Al_2O_3 \cdot H_2O$) such as Boehmite, diaspore; aluminum hydroxide [$Al(OH)_3$] such as gibbsite, bayerite; aluminum carbonate [$Al_2(CO_3)_3$]; magnesium hydroxide [$Mg(OH)_2$]; magnesium oxide (MgO); magnesium carbonate ($MgCO_3$); talc ($3MgO \cdot 4SiO_2 \cdot H_2O$); attapulgite ($5MgO \cdot 8SiO_2 \cdot 9H_2O$); titanium white (TiO_2); titanium black (TiO_{2n-1}); calcium oxide (CaO); calcium hydroxide [$Ca(OH)_2$]; magnesium aluminum oxide ($MgO \cdot Al_2O_3$); clay ($Al_2O_3 \cdot 2SiO_2$); kaolin ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$); pyrophyllite ($Al_2O_3 \cdot 4SiO_2 \cdot H_2O$); bentonite ($Al_2O_3 \cdot 4SiO_2 \cdot 2H_2O$); aluminum silicate ($Al_2SiO_5 \cdot Al_4 \cdot 3SiO_4 \cdot 5H_2O$, etc.); magnesium silicate ($Mg_2SiO_4 \cdot MgSiO_3$, etc.); calcium silicate (Ca_2SiO_4 , etc.); calcium-aluminum silicate ($Al_2O_3 \cdot CaO \cdot 2SiO_2$, etc.); calcium magnesium silicate ($CaMgSiO_4$); calcium carbonate ($CaCO_3$); zirconium oxide (ZrO_2); zirconium hydroxide [$ZrO(OH)_2 \cdot nH_2O$]; zirconium carbonate [$Zr(CO_3)_2$]; a crystalline aluminosilicate containing hydrogen, alkaline metal or alkaline earth metal capable of correcting charge, such as various types of zeolite; and the like. Either a single type or combination of two or more types of these examples may be used as the white filler.

[0126] The rubber composition may further include, other than the rubber components and the reinforcing filler, additives conventionally used in the rubber industry such as a vulcanizing agent, a vulcanization auxiliary, a vulcanization accelerator, a softener, an antioxidant, a scorch protection agent, a processing aid, a filler-modifying agent, a tackifier, a foaming agent, a coloring agent, and the like. The order and stage in/at which these additives are added is not particularly limited but a vulcanizing agent is added preferably in the final process. Commercially available products can be used as these additives.

[0127] Our rubber composition described above can be obtained by mixing and kneading a rubber component containing our multiblock copolymer with a reinforcing filler and other necessary additives. Mixing and kneading can be carried out according to a method conventionally implemented to obtain a rubber composition. For example, our rubber composition can be manufactured by: subjecting the rubber component to mastication as required, by using a conventional rubber mixing-kneading device such as a bunbury mixer, a Brabender plastograph, rolls, a kneader, or the like; adding a reinforcing filler and necessary additives other than a vulcanizing agent, zinc oxide and a vulcanization retarder to the rubber component and mixing and kneading the resulting mixture; adding a vulcanizing agent, zinc oxide and a vulcanization retarder and mixing and kneading the resulting mixture; and subjecting the mixture to warming, extrusion and the like according to necessity, although the manufacturing method is not particularly limited thereto.

[Tire]

[0128] Type of our tire is not particularly restricted as long as the tire uses our rubber composition described above and may be appropriately selected according to the purpose. Our tire can be manufactured by a conventional method. For example, our tire can be manufactured as desired by: sequentially stacking structural members generally for use in manufacturing a tire such as a carcass layer, a belt layer and a tread layer, made of the unvulcanized rubber composition, on a tire building drum; pulling the drum out to obtain a green tire; and subjecting the green tire to heating and vulcanization according to the conventional method. Conditions of heating and vulcanization are not particularly restricted and may be appropriately selected according to the purpose but preferably the temperature is kept in the range of 130°C to 200°C and the heating time is set in the range of 1 minute to 60 minutes.

EXAMPLES

[0129] Hereinafter, the present disclosure will be described more in detail by Examples and Comparative Examples. These Examples and Comparative Examples, however, do not restrict by any means the present disclosure.

[Synthesis of multiblock copolymer]

[0130] Multiblock copolymers for use in Examples and Comparative Examples were synthesized as described in the following Synthesis Examples.

< Synthesis Example 1: Multiblock copolymer EBR1 >

[0131] 250 g of toluene solution was charged into a dry 1L pressure-resistant stainless reactor and then ethylene was introduced thereto at 1.5 MPa to obtain a polymerization solution. 46.1 μmol of bis(2-phenylindenyl)gadolinium bis(dimethylsilyl)amide $[(2\text{-PhC}_9\text{H}_6)_2\text{GdN}(\text{SiHMe}_2)_2]$, 51.0 μmol of N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate $[\text{Me}_2\text{NHPb}(\text{C}_6\text{F}_5)_4]$, and 0.70 ml of diisobutylaluminum hydride were charged into a glass vessel in a glovebox under nitrogen atmosphere and these substances were dissolved in 20 mL of toluene, to obtain a catalyst solution. The catalyst solution was collected from the glovebox and the whole amount thereof was added to the polymerization solution. Thereafter, a toluene solution containing 1,3-butadiene was continuously added to the mixture for 130 minutes at a flow rate of 2 g/minute (in terms of 1,3-butadiene) and polymerization was allowed to continue for 10 more minutes. The polymerization reaction was then stopped by adding 2 mL isopropanol solution of 5 mass % 2,2-methylene-bis(4-ethyl-6-t-butylphenol) (NS-5) after polymerization was completed. A large amount of methanol was added to isolate copolymer and the copolymer thus isolated was vacuum-dried at 70 °C, whereby multiblock copolymer EBR1 was obtained. The yield of EBR1 thus obtained was 52.0 g.

< Synthesis Example 2: Multiblock copolymer EBR2 >

[0132] 200 g of toluene solution was charged into a dry 1L pressure-resistant stainless reactor and then ethylene was introduced thereto at 1.5 MPa to obtain a polymerization solution. 46.1 μmol of bis(2-phenylindenyl)gadolinium bis(dimethylsilyl)amide $[(2\text{-PhC}_9\text{H}_6)_2\text{GdN}(\text{SiHMe}_2)_2]$, 51.0 μmol of N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate $[\text{Me}_2\text{NHPb}(\text{C}_6\text{F}_5)_4]$, and 0.55 ml of diisobutylaluminum hydride were charged into a glass vessel in a glovebox under nitrogen atmosphere and these substances were dissolved in 20 mL of toluene, to obtain a catalyst solution. The catalyst solution was collected from the glovebox and the whole amount thereof was added to the polymerization solution. Thereafter, a toluene solution containing 1,3-butadiene was continuously added to the mixture for 170 minutes at a flow rate of 2 g/minute (in terms of 1,3-butadiene) and polymerization was allowed to continue for 10 more minutes. The polymerization reaction was then stopped by adding 2 mL isopropanol solution of 5 mass % 2,2-methylene-bis(4-ethyl-6-t-butylphenol) (NS-5) after polymerization was completed. A large amount of methanol was added to isolate copolymer and the copolymer thus isolated was vacuum-dried at 70 °C, whereby multiblock copolymer EBR2 was obtained. The yield of EBR2 thus obtained was 83.0 g.

< Synthesis Example 3: Multiblock copolymer EBR3 >

[0133] 200 g of toluene solution was charged into a dry 1L pressure-resistant stainless reactor and then ethylene was introduced thereto at 1.5 MPa to obtain a polymerization solution. 46.1 μmol of bis(2-phenylindenyl)gadolinium bis(dimethylsilyl)amide $[(2\text{-PhC}_9\text{H}_6)_2\text{GdN}(\text{SiHMe}_2)_2]$, 51.0 μmol of N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate $[\text{Me}_2\text{NHPb}(\text{C}_6\text{F}_5)_4]$, and 0.70 ml of diisobutylaluminum hydride were charged into a glass vessel in a glovebox under nitrogen atmosphere and these substances were dissolved in 20 mL of toluene, to obtain a catalyst solution. The catalyst solution was collected from the glovebox and the whole amount thereof was added to the polymerization solution. Thereafter, a toluene solution containing 1,3-butadiene was continuously added to the mixture for 130 minutes at a flow rate of 2 g/minute (in terms of 1,3-butadiene) and polymerization was allowed to continue for 10 more minutes. The polymerization reaction was then stopped by adding 2 mL isopropanol solution of 5 mass % 2,2-methylene-bis(4-ethyl-6-t-butylphenol) (NS-5) after polymerization was completed. A large amount of methanol was added to isolate copolymer and the copolymer thus isolated was vacuum-dried at 70 °C, whereby multiblock copolymer EBR3 was obtained. The yield of EBR3 thus obtained was 85.0 g.

< Synthesis Example 4: Multiblock copolymer EBR4 >

[0134] 200 g of toluene solution was charged into a dry 1L pressure-resistant stainless reactor and then ethylene was

introduced thereto at 1.6 MPa to obtain a polymerization solution. 46.1 μmol of bis(2-phenylindenyl)gadolinium bis(dimethylsilyl)amide $[(2\text{-PhC}_9\text{H}_6)_2\text{GdN}(\text{SiHMe}_2)_2]$, 51.0 μmol of N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate $[\text{Me}_2\text{NHPb}(\text{C}_6\text{F}_5)_4]$, and 0.80 ml of diisobutylaluminum hydride were charged into a glass vessel in a glovebox under nitrogen atmosphere and these substances were dissolved in 20 mL of toluene, to obtain a catalyst solution. The catalyst solution was collected from the glovebox and the whole amount thereof was added to the polymerization solution. Thereafter, a toluene solution containing 1,3-butadiene was continuously added to the mixture for 180 minutes at a flow rate of 2 g/minute (in terms of 1,3-butadiene) and polymerization was allowed to continue for 10 more minutes. The polymerization reaction was then stopped by adding 2 mL isopropanol solution of 5 mass % 2,2-methylene-bis(4-ethyl-6-t-butylphenol) (NS-5) after polymerization was completed. A large amount of methanol was added to isolate copolymer and the copolymer thus isolated was vacuum-dried at 70 °C, whereby multiblock copolymer EBR4 was obtained. The yield of EBR4 thus obtained was 84.4 g.

< Synthesis Example 5: Multiblock copolymer EBR5 >

[0135] 200 g of toluene solution was charged into a dry 1L pressure-resistant stainless reactor and then ethylene was introduced thereto at 1.3 MPa to obtain a polymerization solution. 62.5 μmol of bis(2-phenylindenyl)gadolinium bis(dimethylsilyl)amide $[(2\text{-PhC}_9\text{H}_6)_2\text{GdN}(\text{SiHMe}_2)_2]$, 69.0 μmol of N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate $[\text{Me}_2\text{NHPb}(\text{C}_6\text{F}_5)_4]$, and 0.80 ml of diisobutylaluminum hydride were charged into a glass vessel in a glovebox under nitrogen atmosphere and these substances were dissolved in 20 mL of toluene, to obtain a catalyst solution. The catalyst solution was collected from the glovebox and the whole amount thereof was added to the polymerization solution. Thereafter, a toluene solution containing 1,3-butadiene was continuously added to the mixture for 240 minutes at a flow rate of 1.4 g/minute (in terms of 1,3-butadiene) and polymerization was allowed to continue for 10 more minutes. The polymerization reaction was then stopped by adding 2 mL isopropanol solution of 5 mass % 2,2-methylene-bis(4-ethyl-6-t-butylphenol) (NS-5) after polymerization was completed. A large amount of methanol was added to isolate copolymer and the copolymer thus isolated was vacuum-dried at 70 °C, whereby multiblock copolymer EBR5 was obtained. The yield of EBR5 thus obtained was 95.3 g.

< Synthesis Example 6: Multiblock copolymer EBR6 >

[0136] 2,000 g of toluene solution containing 230 g (4.26 mol) of 1,3-butadiene was charged into a dry 4L stainless reactor and then ethylene was introduced thereto at 1.72 MPa to obtain a polymerization solution. 145 μmol of bis(2-phenylindenyl)gadolinium bis(dimethylsilyl)amide $[(2\text{-PhC}_9\text{H}_6)_2\text{GdN}(\text{SiHMe}_2)_2]$, 145 μmol of N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate $[\text{Me}_2\text{NHPb}(\text{C}_6\text{F}_5)_4]$, and 2.9 mmol of diisobutylaluminum hydride were charged into a glass vessel in a glovebox under nitrogen atmosphere and these substances were dissolved in 100 mL of toluene, to obtain a catalyst solution. The catalyst solution was collected from the glovebox and a portion thereof, equivalent to 142 μmol in terms of gadolinium, was added to the polymerization solution. Polymerization was allowed to proceed at 60 °C for 60 minutes. The polymerization reaction was then stopped by adding 5 mL isopropanol solution of 5 mass % 2,2-methylene-bis(4-ethyl-6-t-butylphenol) (NS-5) after polymerization was completed. A large amount of methanol was added to isolate copolymer and the copolymer thus isolated was vacuum-dried at 70 °C, whereby multiblock copolymer EBR6 was obtained. The yield of EBR6 thus obtained was 248 g.

< Synthesis Example 7: Random copolymer EBR7 >

[0137] 2,000 g of toluene solution containing 200 g (3.70 mol) of 1,3-butadiene was charged into a dry 4L stainless reactor and then ethylene was introduced thereto at 1.72 MPa to obtain a polymerization solution. 45 μmol of mono(tribenzylsilylindene)gadolinium bis[di(trimethylsilyl)amide] $[(\text{C}_6\text{H}_5\text{CH}_2)_3\text{SiC}_9\text{H}_6]\text{Gd}[\text{N}(\text{SiMe}_3)_2]_2$, 47 μmol of N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate $[\text{Me}_2\text{NHPb}(\text{C}_6\text{F}_5)_4]$, and 0.9 mmol of diisobutylaluminum hydride were charged into a glass vessel in a glovebox under nitrogen atmosphere and these substances were dissolved in 100 mL of toluene, to obtain a catalyst solution. The catalyst solution was collected from the glovebox and the whole amount thereof was added to the polymerization solution. Polymerization was allowed to proceed at 100 °C for 180 minutes. The polymerization reaction was then

[0138] stopped by adding 5 mL isopropanol solution of 5 mass % 2,2-methylene-bis(4-ethyl-6-t-butylphenol) (NS-5) after polymerization was completed. A large amount of methanol was added to isolate copolymer and the copolymer thus isolated was vacuum-dried at 70 °C, whereby random copolymer EBR7 was obtained. The yield of EBR7 thus obtained was 147.5 g. Crystal content of the non-conjugated olefin portion of EBR7, determined by TD-NMR described below, was zero, whereby it was confirmed that copolymer EBR7 was random copolymer.

< Synthesis Example 8: Multiblock copolymer EBR8 >

[0139] 200 g of toluene solution was charged into a dry 1L pressure-resistant stainless reactor and then ethylene was introduced thereto at 1.5 MPa to obtain a polymerization solution. 55.1 μmol of bis(2-phenylindenyl)gadolinium bis(dimethylsilyl)amide $[(2\text{-PhC}_9\text{H}_6)_2\text{GdN}(\text{SiHMe}_2)_2]$, 61.0 μmol of N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate $[\text{Me}_2\text{NHPb}(\text{C}_6\text{F}_5)_4]$, and 0.80 ml of diisobutylaluminum hydride were charged into a glass vessel in a glovebox under nitrogen atmosphere and these substances were dissolved in 20 mL of toluene, to obtain a catalyst solution. The catalyst solution was collected from the glovebox and the whole amount thereof was added to the polymerization solution. Thereafter, a toluene solution containing 1,3-butadiene was continuously added to the mixture for 156 minutes at a flow rate of 2.0 g/minute (in terms of 1,3-butadiene) and polymerization was allowed to continue for 10 more minutes. The polymerization reaction was then stopped by adding 2 mL isopropanol solution of 5 mass % 2,2-methylene-bis(4-ethyl-6-t-butylphenol) (NS-5) after polymerization was completed. A large amount of methanol was added to isolate copolymer and the copolymer thus isolated was vacuum-dried at 70 °C, whereby multiblock copolymer EBR8 was obtained. The yield of EBR8 thus obtained was 77.4 g.

< Synthesis Example 9: Multiblock copolymer EBR9 >

[0140] 250 g of toluene solution was charged into a dry 1L pressure-resistant stainless reactor and then ethylene was introduced thereto at 1.7 MPa to obtain a polymerization solution. 46.1 μmol of bis(2-phenylindenyl)gadolinium bis(dimethylsilyl)amide $[(2\text{-PhC}_9\text{H}_6)_2\text{GdN}(\text{SiHMe}_2)_2]$, 51.0 μmol of N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate $[\text{Me}_2\text{NHPb}(\text{C}_6\text{F}_5)_4]$, and 0.70 ml of diisobutylaluminum hydride were charged into a glass vessel in a glovebox under nitrogen atmosphere and these substances were dissolved in 21 mL of toluene, to obtain a catalyst solution. The catalyst solution was collected from the glovebox and the whole amount thereof was added to the polymerization solution. Thereafter, a toluene solution containing 1,3-butadiene was continuously added to the mixture for 190 minutes at a flow rate of 1.4 g/minute (in terms of 1,3-butadiene) and polymerization was allowed to continue for 10 more minutes. The polymerization reaction was then stopped by adding 2 mL isopropanol solution of 5 mass % 2,2-methylene-bis(4-ethyl-6-t-butylphenol) (NS-5) after polymerization was completed. A large amount of methanol was added to isolate copolymer and the copolymer thus isolated was vacuum-dried at 70 °C, whereby multiblock copolymer EBR9 was obtained. The yield of EBR9 thus obtained was 79.4 g.

[Physical properties of polymers]

[0141] Content of a non-conjugated olefin portion and crystal content of the non-conjugated olefin portion were measured for each of the copolymers synthesized in the aforementioned Synthesis Examples, whereby it was confirmed that the copolymers, other than EBR7, are unanimously multiblock copolymers of ethylene and butadiene. Further, degree of crystallinity of the non-conjugated olefin portion and the weight average molecular weight in terms of polystyrene were determined for each of the copolymers. The weight average molecular weight in terms of polystyrene was also determined for butadiene rubber for use in Comparative Examples 1, 3. Regarding a polyethylene/butadiene mixture for use in Comparative Example 3, content of a polyethylene portion in the whole mixture, crystal content and degree of crystallinity of the polyethylene portion, and the weight average molecular weight in terms of polystyrene of the whole mixture, were determined based on the mixture ratio of polyethylene. The methods for determining (i.e. measuring and calculating) the aforementioned physical properties are as follows.

< Content of non-conjugated olefin portion >

[0142] Content (mol %) of a non-conjugated olefin portion of each multiblock copolymer thus synthesized was determined by: measuring ^{13}C -NMR spectra of the multiblock copolymer; and obtaining an integration ratio of a peak derived from a non-conjugated olefin block and a peak derived from a conjugated diene compound block, to calculate content of the non-conjugated olefin portion based on the integration ratio. A peak derived from a non-conjugated olefin block appears around 29-30 ppm and a peak derived from a conjugated diene compound block appears around 27-28 ppm in ^{13}C -NMR spectra.

< Crystal content of non-conjugated olefin portion >

[0143] Crystal content (mol %) of a non-conjugated olefin portion of each multiblock copolymer thus synthesized was determined by using NMR or specifically by: measuring a FID (free induction decay) signal, for the multiblock copolymer, by using a time-domain NMR (TD-NMR) analyzer according to the MSE (magic sandwich echo) method; and subjecting the FID signal to fitting by an analytical equation, to estimate crystal content (f_c) of the non-conjugated olefin portion

of the multiblock copolymer. The analytical equation shown below was used for fitting.

$$G(t) = f_c \cdot \exp\{-0.5(at)^2\} \cdot \sin(bt)/bt + f_i \cdot e^{(t/T_{2i})^{1/v_a}} + f_m \cdot e^{(t/T_{2m})^{1/v_i}}$$

wherein $f_c + f_i + f_m = 1$,

f_c : proportion of crystals of a non-conjugated olefin portion (1 H%),

f_i : proportion of intermediate phase (1 H%), and

f_m : proportion of soft phase (1 H%)

[0144] Setting of a pulse program and an analytical method associated therewith were based on the teachings described in the following reference: Kerstin Schaefer, *Macromolecules* 2013, 46, pp. 7818-7825; and Henriette W. Meyer, *Polymer Journal* (2012) 44, pp. 748-756.

[0145] The respective crystal contents of the non-conjugated olefin portions thus determined for EBR1-EBR6, EBR8 and EBR9 unanimously exceeded zero, whereby it was confirmed that EBR1-EBR6, EBR8 and EBR9 are unanimously ethylene-butadiene multiblock copolymer.

< Degree of crystallinity of non-conjugated olefin portion >

[0146] Degree of crystallinity (%) of a non-conjugated olefin portion was calculated by the following formula for each multiblock copolymer thus synthesized.

$$\text{Degree of crystallinity of non-conjugated olefin portion} = (\text{Crystal content of the non-conjugated olefin portion} / \text{Content of the non-conjugated olefin portion}) \times 100$$

< Weight average molecular weight in terms of polystyrene >

[0147] The weight average molecular weight in terms of polystyrene was determined according to gel permeation chromatography (GPC) by using polystyrene as the standard substance.

[Evaluation method]

[0148] Rubber compositions of Examples and Comparative Examples, respectively prepared according to the blending ratios shown in Table 1, were each vulcanized and crack resistance and fracture resistance of a vulcanized rubber sample thus obtained was evaluated. Evaluation methods are as follows. The evaluation results are shown, together with the relevant physical properties, in Table 2.

< Resistance to crack growth >

[0149] Resistance to crack growth was determined by: subjecting each vulcanized rubber sample to aging at 100 °C for 24 hours according to JIS K6257; forming a crack (0.5 mm) at the center portion of a JIS No. 3 test piece cut out from the sample; subjecting the test piece to fatigue repeatedly at 60 °C under 0% to 100% strain; counting the number of subjecting the test piece to fatigue before the test piece was broken; and expressing the number thus counted by an index value relative to the number of Comparative Example 1 being "100". The larger index value represents the higher resistance to crack growth after being aged.

< Fracture resistance >

[0150] Fracture resistance was determined by: subjecting each vulcanized rubber sample to a tensile test according to JIS K6251, to measure tensile strength at fracture (rupture) and elongation at fracture (rupture) at the room temperature; calculating a fracture resistance value by the following equation, based on the tensile strength and elongation at fracture (rupture) thus measured; and expressing the fracture resistance value by an index value relative to the fracture resistance value of Comparative Example 1 being "100". The larger index value represents the higher fracture resistance.

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$$(\text{Fracture resistance value}) = (\text{Tensile strength at fracture}) \times (\text{Elongation at fracture})/2$$

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[Table 2]

Table 2	Examples										Comparative Examples					
	1	2	3	4	5	6	1	2	3	4	5	1	2	3	4	5
Rubber Component*1	EBR1	EBR2	EBR3	EBR4	EBR8	EBR9	BR	EBR5	PE/BR	EBR6	EBR7	BR	EBR5	PE/BR	EBR6	EBR7
Content of non-conjugated olefin portion [mol %]*2	9	25	39	39	16	45	0	53	0 (25)	36	15	0	53	0 (25)	36	15
Crystal content of non-conjugated olefin portion [mol %]*3	1	4	8	14	2	18	0	23	0 (14)	23	0	0	23	0 (14)	23	0
Degree of crystallinity of non-conjugated olefin portion [%]*4	11	16	21	36	13	40	0	43	0 (56)	64	0	0	43	0 (56)	64	0
Weight average molecular weight in terms of polystyrene [$\times 10^3$]	420	350	400	405	390	370	550	390	550	430	380	550	390	550	430	380
Evaluation	Crack resistance (Index)	240	460	2500	590	320	100	300	50	20	140	100	300	50	20	140
	Fracture resistance (Index)	100	145	145	120	120	100	70	60	81	90	100	70	60	81	90

*1) EBR1-6, EBR8 and EBR9: Ethylene-butadiene multiblock copolymer, EBR7: Ethylene-butadiene random copolymer

BR: Butadiene rubber, PE/BR: Polyethylene/butadiene rubber mixture

*2) The value in brackets represents the content of non-conjugated olefin polymer in the whole mixture.

*3) The value in brackets represents the crystal content of non-conjugated olefin polymer in the whole mixture.

*4) The value in brackets represents the degree of crystallinity of non-conjugated olefin polymer in the whole mixture.

[0151] It is understood from the results shown in Table 2 that the rubber compositions of Examples, each containing our multiblock copolymer as a rubber component, exhibit higher fracture resistance and higher resistance to crack growth than the rubber compositions of Comparative Examples. High fracture resistance represents a good effect of preventing cracks from being generated and high resistance to crack growth represents a good effect of preventing cracks from further growing. That is, being excellent in fracture resistance and resistance to crack growth represents being excellent in crack resistance. It is therefore possible to obtain vulcanized rubber having high fracture resistance and high crack resistance by using our rubber composition. For the same reason, a tire using our rubber composition exhibits high fracture resistance and high crack resistance.

INDUSTRIAL APPLICABILITY

[0152] Our multiblock copolymer is preferable for use in a rubber product requiring high fracture resistance and high crack resistance, for example, a rubber composition for a tire material or the like. Further, our rubber composition is preferable for use in a rubber product requiring high fracture resistance and high crack resistance, for example, a tire or the like.

Claims

1. A multiblock copolymer, obtainable by copolymerization of a conjugated diene compound and a non-conjugated olefin, wherein:

a structure of the multiblock copolymer includes $A-(B-A)_x$ and/or $B-(A-B)_x$, wherein "A" represents a block portion constituted of monomer units of a non-conjugated olefin, "B" represents a block portion constituted of monomer units of a conjugated diene compound, and "x" represents an integer ≥ 1 ;
 content of the non-conjugated olefin portion is ≤ 50 mol %;
 $0 \text{ mol \%} < \text{crystal content of the non-conjugated olefin portion} \leq 20 \text{ mol \%}$; and
 $0 \% < \text{degree of crystallinity of the non-conjugated olefin portion} \leq 40 \%$.

2. The multiblock copolymer of claim 1, wherein the content of the non-conjugated olefin portion is in the range of 10 mol % to 40 mol %.

3. The multiblock copolymer of claim 1 or 2, wherein the crystal content of the non-conjugated olefin portion is in the range of 5 mol % to 15 mol %.

4. The multiblock copolymer of any of claims 1 to 3, wherein the degree of crystallinity of the non-conjugated olefin portion is in the range of 15 % to 40 %.

5. A rubber composition, having as a rubber component the multiblock copolymer of any of claims 1 to 4.

6. A tire, having the rubber composition of claim 5.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2015/000923

A. CLASSIFICATION OF SUBJECT MATTER

C08F297/06(2006.01)i, B60C1/00(2006.01)i, B60C9/04(2006.01)i, B60C9/20
(2006.01)i, B60C11/00(2006.01)i, C08L53/00(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08F297/06-297/08, C08L53/00, C08L21/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2015
Kokai Jitsuyo Shinan Koho 1971-2015 Toroku Jitsuyo Shinan Koho 1994-2015

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2012/014457 A1 (Bridgestone Corp.), 02 February 2012 (02.02.2012), claims; paragraphs [0025], [0027] to [0093], [0101], [0103] to [0125] & US 2013/0211010 A1 & EP 2599809 A1 & CN 103154061 A & RU 2013108954 A	1-6
A	JP 2013-79338 A (Bridgestone Corp.), 02 May 2013 (02.05.2013), claims; paragraphs [0023], [0028] to [0038], [0044] to [0130], [0146] to [0163] (Family: none)	1-6

Further documents are listed in the continuation of Box C. See patent family annex.

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Date of the actual completion of the international search
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2015/000923

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2012/014420 A1 (Bridgestone Corp.), 02 February 2012 (02.02.2012), claims; paragraphs [0013] to [0107] & US 2013/0211032 A1 & EP 2599808 A1 & CN 103140521 A & RU 2013108956 A	1-6
A	WO 2012/164914 A1 (Bridgestone Corp.), 06 December 2012 (06.12.2012), claims; paragraphs [0024] to [0095], [0103] to [0128] & US 2014/0179861 A & EP 2716670 A1 & CN 103562246 A	1-6
A	JP 2013-133373 A (Bridgestone Corp.), 08 July 2013 (08.07.2013), claims; paragraphs [0011] to [0115], [0125] to [0140] (Family: none)	1-6

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- US 4645793 A [0003]

Non-patent literature cited in the description

- **KERSTIN SCHAELE**R. *Macromolecules*, 2013, vol. 46, 7818-7825 [0019] [0144]
- **HENRIETTE W. MEYER**. *Polymer Journal*, 2012, vol. 44, 748-756 [0019] [0144]